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BATTERY ACTIVE NICKEL OXIDES

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ABSTRACT

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A literature review of recent articles dealing with the chemical structure and composition of the nickel oxide electrode is presented. The entire program for this project is outlined, and the work completed during the first quarter is discussed. Sintered plate nickel oxide electrodes completed all formation cycling. Initial data for self discharge stand is given for 10, 25 and 50°C. X-ray diffraction patterns of the charged nickel oxide electrodes are given.

Author

I. INTRODUCTION

A. PURPOSE

Work performed under this contract will be directed (1) toward an identification of the nickel oxide compounds formed during charge of the electrode; (2) to determine when they are formed; (3) to determine which factors (such as current density and temperature) affect the charge process; (4) to relate the shelf-loss process to these compounds, and (5) to determine the compounds which disappear during discharge of these electrodes.

After the forms of nickel oxide present have been established, a further effort will be directed toward stabilization of the nickel oxides during high temperature stand.

B. MEETINGS

On September 1, 1964, a meeting was held with Mr. W. Nagel of NASA Lewis. Messrs. M. Lurie, P. Ritterman and Drs. R. C. Shair and H. N. Seiger represented Gulton Industries. The meeting took place at Gulton Industries, Metuchen, New Jersey.

The following was decided:

1. In general, the work plan will continue as scheduled.
2. An additional series of experiments will be run to determine if there is any difference in the characteristics of the positive electrode between a sealed and vented charge.
3. The effects of several atmospheres on differential thermal analysis will be included in the program. These will be inert, oxidizing and reducing atmospheres.

C. LITERATURE SEARCH

1. Bibliography

The following articles constitute the bibliography on electrochemically formed nickel oxides.

a. Investigation of the Sintered Plate Nickel-Cadmium Battery.
Final Report - Sandia Corp. - 1958
A. J. Salkind, P. F. Bruins

b. Nickel-Cadmium Cells I. Thermodynamics and X-Ray Studies
A. J. Salkind, P. F. Bruins J. of Electrochemical Soc.
Vol. 109 No. 5 P. 356-360

c. Investigations on the Reaction Mechanism of the Nickel-Cadmium Cell. S. Uno Falk - J. Electrochemical Soc.
Vol. 107 No. 8 P. 661-667

d. X-Ray Studies of Divalent and Trivalent Nickel Compounds
Cairns and Ott. J. American Chemical Soc. 55, 527 (1933)
and 55, 533 (1933)

e. The Structure of Higher Nickel Hydroxides
Glemser and Einerhand - Zeitschrift Fur Anorganische Cheme
261 (1950) P. 43-51

f. Chemical Processes at the Electrodes of Electrochemical Sources of Current. H. Bode - Angew. Chem. 73 (1961)
553-60

g. The Significance of EMF Decay Measurement; Application to Nickel Oxide Electrode. Conway and Bourgault.
Trans. Faraday Society 58, 593-607 (1962)

h. Open Circuit Studies Highly Oxidized NiO Surface Absorbed O_2 Radicals - Conway and Bourgault Canadian Journal of Chemistry 38, (1960) 1557-75.

i. Alkaline Storage Batteries - the Self Discharge of the Positively Charged Nickel Oxide Electrode Pitman and Work - Naval Research Laboratory NRL report 4844, 4845.

j. H. N. Seiger and R. C. Shair, Paper presented at the Electrochemical Society Meeting, Fall, 1962, Detroit.

k. The Nickel Oxide Electrode - 3. G. W. D. Briggs and W. F. K. Wynne Jones - Trans. of Faraday Society No. 405, Vol. 59 (1956) 1272 - 1281.

l. The Higher Nickel Hydroxide; the Oxidation of Nickel II Hydroxide. Feitknecht, Christen and Studer. Z. Anorg. U. Allgem. Chem. 283 (1956) P. 88-95.

2. Review of Literature

Although various exotic compounds of nickel, oxygen and hydrogen were discussed and prepared by Cairn and Ott, Glemser and Einerhand and a number of other investigators, it was never stated that these were found to correspond to any particular state-of-charge of the positive plate. For the most part these authors (Cairns, Ott, Glemser, Einerhand) concentrated on the chemical oxidation of nickel hydroxide rather than electrochemical.

Compounds which were claimed to have been found due to charge and discharge of a nickel hydroxide electrode are NiOOH, $Ni_2O_3 \cdot 2H_2O$, $Ni_2O_3 \cdot H_2O$, $Ni(OH)_2$, $Ni_3O_2(OH)_4$, δ NiOOH

The most recent works on this subject were by Salkind and Bruins and Uno Falk. These authors present data indicating only β NiOOH and $Ni(OH)_2$ under ordinary charge and discharge conditions. Under extreme overcharge conditions Salkind found that $Ni_2O_3 \cdot H_2O$ is also formed. These results were obtained at various states of charge and temperatures by x-ray diffraction measurement. There is a discrepancy between Salkind and Falk on the one hand, and other authors which the former investigators attributed to different procedures used in preparing the positive plates for x-ray analysis. Salkind and Falk arranged special cells which enabled x-ray work to be done on plates wet with hydroxide. The other authors washed and dried their plates which could have caused the formation of other nickel oxide compounds.

The "graphitic" level, or second discharge level, corresponding to a plateau at a cell voltage of 0.7 volts has been hypothesized as $Ni_3O_2(OH)_4$. This compound, however, was not found by Falk or Salkind at any state-of-charge.

The existance of higher oxides help explain an excess capacity of 10% - 15% found upon discharge of freshly charged plates. The workers about the turn of the century, and more recently Bode, have speculated the existance of the unstable and amorphous compound NiO_2.

The work of Pitman and Work attribute the 10% excess capacity to adsorbed oxygen. They also claim that the so-called "graphitic" level is due to adsorbed oxygen on the discharged $Ni(OH)_2$.

Conway and Bourgault attribute the excess capacity to a monolayer surface phase of adsorbed oxygen-containing radials such as O, OH on the conducting metal surface, or a higher oxide of nickel. They found that the volume of oxygen evolved from this phase corresponds to less than a monolayer of surface.

In this laboratory it was shown that upon charge there are formed unstable compounds. One of the "compounds" may be adsorbed oxygen. No direct relationship between the potential and oxygen evolution rate was found. Recently, workers here have suggested a kinetic approach which may resolve the oxygen loss on stand with potential.

To summarize: Recent work indicates that $Ni(OH)_2$ and β NiOOH are the only compounds existing in the positive electrode of a nickel-cadmium battery. Increased electrochemical capacity is probably due to adsorbed oxygen.

II. OUTLINE OF PROGRAM

The program is divided into three phases. It is being carried out using both sintered plate and tubular positive electrodes. Tubular electrodes with graphite as the only contaminate can be readily analyzed chemically. This avoids the unknowns introduced by use of a nickel base. It is especially important when analyzing compounds which are unstable, and consequently require rapid separation.

A. PHASE 1.

1. Literature Survey

A review was made of current literature pertaining to structure of the nickel oxide electrode. The review appeared in Section I-C above.

2. Construction of Test Cells

a. Plates

Positive plates manufactured entirely by Gulton Industries will be used.

i) Sintered Plates - Sintered plates will all be impregnated at the same time with $Ni(NO_3)_2$ which will then be converted chemically to $Ni(OH)_2$.

ii) Pocket Plates - $Ni(OH)_2$ will be prepared from the same batch of $Ni(NO_3)_2$ used in impregnation of sintered plates. The $Ni(OH)_2$ will be mixed with graphite and packed into stainless steel pockets.

b. Cell Stacks

Positive plates will be combined with sintered plate negative electrodes to form cores or stacks. The core configuration will be two positive and three negative for the sintered type, one positive and two

negatives for the pocket type.

3. Treatment

Thirty cores of each type will be constructed and cycled using 34% KOH as electrolyte via the following regime.

a. Shorted to V = 0 for 24 hours.

b. Constant current charge 140% at 5 hour rate.

c. Discharge at 3 hour rate to 0 volts.

This cycle will be repeated five times.

Twenty-one cells closest in capacity based on results of the 5th. cycle will be chosen from each group of 30. These in turn will be divided into highest, middle and lowest thirds. Seven 3 cell groups will be made with one cell from each third per group.

All of the above cells will be charged at C/10 to 200% of capacity in a mineral oil bath at 25°C.

One group will have its positives analyzed 24 hours following charge. Two groups will be cooled to 10°C, two heated to 50°C, and two remain at 25°C. After a 24 hour stand, one group of cells at 50°C and one group at 10°C will be discharged at the 3 hour rate to V = 1.25V and their positives analyzed. The remaining groups will stand, covered to avoid formation of carbonates, at their respective temperatures for 3 months. At this time the positive plates will be analyzed.

4. Methods of Analysis

The positive plates will be analyzed by chemical means, x-ray diffraction, differential thermal analysis, and spectrographically.

a. Chemical Means

The compounds of nickel existing on the positive plate can consist only of nickel, oxygen and hydrogen in varying proportion. By quantitative determination the formula weight of the compound type $Ni_x O_y H_z$ can be determined. Chemical analysis will be made only on the pocket plates for the reasons stated previously.

The following determinations will be made:

i. Total Hydroxide - After removal from the cell the positive plate will be wiped dry of external KOH, allowed to drain by gravity and then opened. An aliquot of the poxitive mix will be placed in a flask and titrated with standard sulfuric acid.

ii. Hydroxide Due to KOH - Another sample is treated as above except that it will be leached and the solid material filtered off. The remaining liquid is titrated with sulfuric acid.

iii. Oxygen - A third sample will be washed and dried, weighed and then dissolved in H_2SO_4 and HI. The liberated iodine will be titrated with $Na_2S_2O_3$.

iv. Nickel - A fourth sample will be washed, dried, weighed and then dissolved in acid. After adjusting pH the Ni^{+2} is precipitated from basic solution with dimethylglyoxime.

v. Hydrogen - A fifth sample will be washed, dried, weighed, mixed with K_2CrO_4 and $PbCrO_4$ and heated to 600°C. The water vapor then produced will be captured in a weighed drying tube.

b. X-Ray Diffraction

Both the sintered and pocket plates will be investigated using x-ray diffraction. Samples will be run both "wet" and dry. The wet samples are those taken out of the cell and wrapped with polyethylene. The dry samples are vacuum dried before x-ray analysis. After an x-ray pattern is taken the d spacings will be calculated and compared to standards.

c. Differential Thermal Analysis

The plate sample is ground to a powder and placed in a stainless steel block containing 3 thermocouples. Another hole in the block contains powdered alumina. The thermocouples are so arranged that there is a response to any reaction or transitional change of the sample. The alumina undergoes no phase change until 2050°C when it melts.

B. PHASE II.

The same type of cores used in Phase I will be employed again. Thirty-six of each type will be made. Charges will be run at the C and C/10 rates. At both these rates, cores will be subjected to the following treatment.

1. Charge to 200% of capacity based on the point at which vigorous gassing is noted off the positive plates equal to 100% charge.

2. Charge another group 10% beyond vigorous gassing point.

3. Charge a third group 20% less than previous groups required to reach vigorous gassing.

4. Charge 200%, discharge leaving 50% of capacity.

5. Charge 200%, discharge leaving 25% of capacity.

6. Charge 200%, discharge to a voltage less than .2 volt versus a Hg/HgO electrode which signifies a fully discharged positive.

A 24 hour stand will be given all these groups before analysis. Three cells will comprise a group. Thus 2 rates x 6 groups x 3 cells/group = 36 cells of the sintered type and 36 cells of the pocket type.

The unstable oxides of nickel must be identified rapidly after cells are charged. For this purpose a 2 plate cell will be prepared. The cell will be assembled within a polyethylene bag. Such a cell fits into the goniometer of Gulton's x-ray diffraction unit. While in the apparatus the cell will be charged at the 1 hour rate.

While in overcharge, when unstable oxides are formed, a diffraction pattern can be made using the G-M counter. When strange lines are found the goniometer can be turned to the appropriate angle for the most pronounced of these lines. Then without scanning, the charge current can be interrupted and the disappearance of the strange line followed with respect to time. By planning a series of these experiments for a reasonable number of the strange lines, and also scanning while the self discharge is occurring, it may then be possible to identify the unstable oxides of nickel. At least the ground-work for such identification will be set.

C. PHASE III.

1. Literature Search

A survey will be made to determine whether oxides or hydroxides similar to those found in the nickel electrode have been stabilized for higher temperature tolerance. It will also determine whether mechanisms of the kind prevalent may be altered by any chemical or physical means.

2. Stable Oxide Synthesis, Test and Analysis

The nickel oxides will be prepared and tested by immersion in alkaline battery electrolyte at 40, 50, and 60°C for a length of time deemed necessary to perceive change in composition. The samples will then be analyzed by the standard techniques before and after soaking.

3. Electrode Preparation and Cell Fabrication

Any method of stable oxide synthesis found successful shall be used to prepare sintered plate nickel oxide electrodes. These electrodes shall be used to fabricate nickel-cadmium test cells. The cells shall be formed as in Phase I by a series of 5 charge-discharge cycles.

4. Stabilized Oxide Cell Testing

Two cells for each stabilization method shall be cycled at 50°C, the cycling to be as above. Similarly, two other cells shall be cycled at 70°C. After testing at these temperatures, the cells shall be cycled again at 25°C for 5 charge-discharge cycles. Then they shall be charged fully and stored for a suitable period of time at 50°C to ascertain the change in rate at which capacity is lost.

III. EXPERIMENTAL RESULTS

A. EXPERIMENTAL PROCEDURE

1. Preparation of Plates

a. Sintered Plates

All sintered plates 0.035" x 2-1/8" x 1-7/8" were impregnated at one time by the continuous impregnation method of Gulton Industries. Each plate gained an average of 2.6 grams as $Ni(OH)_2$.

b. Pocket Plates

From the batch of $Ni(NO_3)_2$ used to impregnate sintered plates described above, a portion was taken and combined with a slight excess of KOH to precipitate $Ni(OH)_2$. The precipitate was washed by decantation and then filtered through Buchner funnel. The precipitate was further washed in the Buchner funnel and then air dried at 50°C for 3 days. The dried precipitate was ground into a powder in a mortar and pestle. Finally it was sifted through a 80 mesh sieve.

The precipitate was combined with number 2M flake graphite obtained from the Asbury Graphite Company in ratio of 7 parts nickel hydroxide to 3 parts graphite. The mixture was ball milled with the mortar and pestle and then wetted with KOH to form a very thick paste. The wet $Ni(OH)_2$ mix was then tamped into a hollow perforated stainless steel cylinder 1/4" O.D. x 4-1/2".

2. Construction of Cells

a. Sintered Plates

Two positive plates were combined with 3 negative plates of the same dimension and with non-woven nylon separator made into a cell core. The core was placed into a plastic container, shimmed tightly and then flooded with 34% KOH electrolyte. Thirty such cells have been constructed.

b. Pocket Plates

Because of difficulty in obtaining conductivity of these plates, which has now been resolved, we have not reached the point of constructing cells from these plates. We are currently building plates.

3. Cycling of Sintered Plate Cells

Since these cells had never seen current, it was decided to give them two constant current charge-discharge cycles. The first cycle involved a 24 hour shorting period followed by a charge at 0.300 amperes for 9 hours. The subsequent discharge was carried out at 0.500 amperes to 0.0 volts. The second cycle started again with a 24 hour short. The second charge was at 0.300 ampere for 7 hours. The second discharge was at 0.500 ampere to 0.0 volts.

After this preliminary cycling the cells received 6 cycles involving a constant load discharge. The 6th. cycle was necessitated by a temporary failure in recording equipment during the previous cycle. Each cycle consisted of a 24 hour

short, a 7 hour charge at 0.300 amps, a discharge through a 2.4 Ω resistor to a voltage approaching zero. Each cell on each cycle was individually discharged through its own 2.4 Ω resistor. Based on the results of the 6th. cycle, 21 cells closest in capacity were chosen out of the group of 30 cells. These were divided into three groups: the first containing those 7 cells with the highest capacity; the second group with those 7 cells having the lowest capacity; and the remaining 7 cells constituted the last group. From these, 7 groups of 3 cells were formed with each group containing a high, middle and low cell.

4. Preparatory Self Discharge Measurements and Analysis of Sintered Plate Cells

The 21 cells selected as described above were placed in an oil bath, kept at 25°C, and they were charged at 0.150 A while thermostatted for a period of 20 hours. One group of three cells was allowed to stand on open circuit for 24 hours at which point these cells were taken apart and the positives of two cells stored at 25°C in KOH in the oil bath. The positives from the third cell were immediately analyzed - one dry and one wet by x-ray diffraction. A dry plate is one which was washed in distilled water and vacuum dried. A wet plate is one which was immediately covered with a polyethylene bag. The other positives were analyzed - one wet, one dry 24 hours afterward, and one 48 hours afterward. Two groups were removed at the end of the 20 hour charge period and stood on open circuit at a temperature of 50°C for 24 hours. At this time one group was discharged at

0.500 A to a voltage of 1.25 volts. The group that was discharged was taken apart. From this point the plates were treated as 25°C runs described above. The undischarged group will remain at 50°C for a period of 3 months, covered to avoid evaporation. Two groups were removed at the end of the 20 hour charge and stood on open circuit at 10°C for 24 hours. One group was discharged to 1.25 volts and also treated at the 25°C described above. The other group will remain on stand at 10°C for 3 months.

5. X-Ray Diffraction Measurements

In addition to the data described above, diffraction patterns have been obtained from $Ni(OH)_2$ unimpregnated plates, polyethylene sheet charged plates and discharged plates.

The general procedure for obtaining an x-ray pattern was as follows:

a. Mount sample on sample holder

b. Set full scale equal to characteristic nickel peaks at 1.76 Angstrom ($2\theta = 51.2^{\circ}$).

c. Set in the 4° collimating slits and set the machine at a sweep rate of 2° per minute. The chart speed is set equal to 30 inches per hour.

d. Calculate "d" spacings by $n\lambda = 2d \sin\theta$

$\lambda = 1.5374$ A (A table had been made of this for each 0.1° step).

6. Differential Thermal Analysis

The differential thermal analysis device employed in this laboratory uses a stainless steel block and three chromel-alumel thermocouples (See Figure 1). One thermocouple in the block records block temperature. The other two are set in polarity opposition to each other and record temperature difference between sample and alumina standard. Samples are powdered and a weighed quantity packed into the sample compartment. When the three hole block with its thermocouples alumina and sample are heated in an oven, a plot of temperature difference versus oven temperature is obtained. This is achieved by attaching the thermocouples from the block to the x-y recorder as shown in Figure 1.

7. Chemical Analysis

Standard solutions for nickel analysis, oxide titration and KOH titration have been prepared.

Ovens and a combustion tube for hydrogen determination have been purchased.

Since the tubular plates have just been prepared, there are no results to report from chemical analysis for this quarter.

B. DATA

1. Cycling of Sintered Plates

The capacities expressed as time in minutes for the two preliminary discharges and the sixth and final constant load discharge cycles are shown in Table I. The capacities are taken to a zero volt cut-off for the first two cycles and

to the knee of the first voltage plateau for the sixth constant load cycle. The letters H, M, L next to cells in Table I indicate that these were selected as the matched capacity curves, and also to which group they were relegated using the letters for "High","Medium" and "Low" capacity. This is based on the sixth constant load cycle.

2. Preparatory Self-Discharge Measurements and Analysis

X-Ray diffraction patterns were taken of positive plates on charged stand at room temperature (25°), elevated temperature (50°C) and cold temperature (10°C). Because only six x-ray patterns could be obtained in one working day, and because we wanted to obtain both "wet" and "dry" patterns at three temperatures for High, Low, and Medium capacity plates, three days were required to obtain all 18 x-ray patterns.

a. Room Temperature - 25°C

The x-ray diffraction pattern for the positive plate of cell 21 was obtained after a 24 hour stand, and appears in Figures 2 and 3. The pattern for plates from cells 5 and 20 which were also analyzed, but on two subsequent days, and their patterns appear in Figures 4 and 5, and 6 and 7 respectively. Figures 2, 4, and 6 represent patterns for "wet" plates. Figures 3, 5, and 7 are patterns obtained from "dry" plates.

b. Elevated Temperature - 50°C

After 24 hours of charged stand at 50°C, cells were discharged at 0.500 ampere to 1.25 volts.

Cell number 27 required 4 minutes to reach that voltage; cell 15 required 5 minutes, and cell 28 needed 6 minutes. This corresponds to cells from the low, medium and high capacity groups respectively.

After discharge the positive plates from cell 28 were immediately analyzed by x-ray diffraction. Twenty-four hours later the positives from cell 15 were analyzed, and 48 hours later those from cell 27 were analyzed. X-ray diffraction patterns appear in Figures 8 and 9, 10 and 11, 12 and 13 respectively. The even numbered figures correspond to wet plate patterns, while the odd numbered figures correspond to dry plate patterns.

c. Low Temperature - 10°C.

After a charged stand at 10°C for 24 hours, cells were discharged at 0.500 ampere to 1.25 volts. All three cells required 7 minutes to reach 1.25 volts.

Plates from cell 24 were immediately x-rayed while plates from cell 10 and 25 were x-rayed 24 and 48 hours later. The x-ray patterns appear in Figures 14 and 15, 16 and 17, 18 and 19 respectively. Again the even numbers correspond to the wet plates and the odd to the dry.

3. Tests of Plates and Nickel Hydroxide by X-ray Analysis

Positive plates of the type described above were charged at the C/6 (100 ma) for 16 hours against excess negative cap-

acity. These represented charged plates. To obtain a discharge plate, a charged plate was shorted through a 1 ohm resistor for 3 hours. Figure 20 shows an x-ray diffraction pattern for an unimpregnated sintered nickel plate (dry). Figure 21 shows an x-ray diffraction pattern for $Ni(OH)_2$ powder.

Figure 22 is the pattern for a single sheet of polyethylene.

The pattern of an unimpregnated sintered plate covered with one layer of polyethylene sheet appears in Figure 23.

Figures 24 and 25 show x-ray patterns of charged plates examined in wet condition covered with polyethylene and in the dry condition respectively.

Figures 26 and 27, respectively, show x-ray patterns for "wet" and "dry" discharged plates.

4. Differential Thermal Analysis

Figure 28 shows an automatic plot of a DTA diagram for $Ni(NO_3)_2 \cdot 6H_2O$. Figure 29 is a plot for $Ba(NO_3)_2$. The melting point and boiling point for $Ni(NO_3)_2 \cdot 6H_2O$ correspond closely to the dips in the curve Figure 28. The dip in Figure 29 occurs at a somewhat higher temperature than the melting point of a $Ba(NO_3)_2$. Figure 30 is a DTA diagram for $Ni(OH)_2$ powder done by dual trace (See Appendix II).

A DTA diagram for NiO powder is shown in Figure 31. Figures 32, 33, and 34 show DTA diagram for discharged plates, the first two with no stand, the third after a 48 hour stand.

Figures 35,36, and 37 show DTA diagram for charged plates, unformed, formed, and after 24 hours stand respectively.

5. Special Test - Tubular Plates

The steel material from which tubular containers were made was subjected to a "charge" at a current density of 25 ma/in.^{2} for 17.5 hours. The samples which weighed about 1.2 grams showed negligible weight losses amounting to less than 6 parts per 10,000. This shows that current does not effect the inert steel part of the tube plates.

C. DISCUSSION

1. Cycling of Sintered Plates

The knee of the first voltage plateau was taken as the point of comparison of cell capacity. As can be seen in the typical discharge curve Figure 38, this represents the only sharp break in the constant load discharge curve. The knee usually occurred at 1.18 volts and dropped sharply to 0.7 volts. The capacity below this point corresponds to the "graphitic" level. This lower level may correspond to absorbed oxygen. The potential of the positive electrode at the cell voltage of 0.7 is about -0.1 to -0.2 volts (Hg/HgO). This is just about the value of potential observed (in this laboratory) for oxygen consumption on a positive electrode via the perhydroxyl mechanism. The theoretical capacity based on the positive plate is equal to 1.5 AH per cell. The average cell voltage during discharge is about 1.2 volts. Hence, for a 2.4 Ω resistor the capacity of each cell expressed in time should be 180 minutes. The actual capacity on the 6th. constant load cycle was lower, due to the cut-off point chosen. As shown by the two constant current discharge

cycles, the actual capacity is less than 100% of theoretical (it is about 85% of this) even when 0 volts is chosen as the cut-off point. Theoretical capacity is usually obtained, however, at lower discharge rates. In this laboratory a C/50 discharge rate will yield theoretical capacity.

2. Preparatory Self-Discharge Measurements and Analysis

a. High Temperature (50°C)

The discharge at 0.500 ampere to 1.25 volts indicates some correlation between overall cell capacity and capacity to 1.25 volts. The low capacity cell required 4 minutes, the middle capacity cell 5 minutes, and the high capacity cell 6 minutes to that voltage.

b. Low Temperature (10°C)

All cells required 7 minutes to reach 1.25 volts when discharged at 0.500 ma. No correlation seems to exist at low temperatures, however, this may be due to the slower self-discharge rate.

c. Preliminary Analysis of X-ray Data

The x-ray data was obtained at the very end of the quarter. Only preliminary analysis of the data was made, but it can be seen that there is considerable difference between x-ray patterns run on wet plates and those run on dry plates. Other observations from the x-ray patterns are that (1) time lag results

in smaller peaks both for wet and dry plates at all temperatures, and (2) different storage temperatures do not seem to effect x-ray patterns a great deal during the initial (first 24 hours) stand.

3. Special Tests - Charged and Discharged Plates

X-ray analyses were run on unimpregnated sintered nickel plates and on nickel hydroxide. These x-ray diffraction patterns, Figures 20, 21 respectively, were used as a calibration for comparison of other plates tested. Table II shows the "d" spacings for these x-rays. Figures 20 and 21 show the "d" spacings and their relative intensities. All x-ray diffraction diagrams of wet plates were observed with the plates encapsulated in polyethylene. An x-ray diffraction diagram of polyethylene is shown in Figure 22, and the determined "d" spacings are listed in Table I. To show that the introduction of polyethylene on a plate does not have any significant effect on the x-ray diffraction diagram of the plate, an x-ray was taken of an unimpregnated sintered nickel plate wrapped in polyethylene and is shown in Figure 23. It can be seen that Figure 23 is a composite of Figures 20 and 22.

Two charged positive plates were tested, the first being removed from the cell wet, and x-rayed, the second being removed from the cell, washed in distilled water, vacuum dried, and then x-rayed. The x-ray diffraction diagrams of the wet and dried plates can be seen in Figures 24 and 25 respectively. The two x-rays are different. Some "d" spac-

ings were present in the wet plate and were not apparent in the dry plate, and the reverse was also true. These differences appeared in the region of "d" spaces greater than 2.03. Additionally, in the wet plate the background was increasing with decreasing "d" spacing, while in the dry plate, the background was essentially constant. These phenomena were present in other wet and dry plates tested.

The x-ray diffraction diagrams for two discharged positive plates are shown in Figures 26 and 27, the former being a wet plate, the latter a dry plate. A comparison of these two x-rays show essentially the same results discussed in the previous paragraph. Since the drying of the plates obviously causes a change in the plates, and for these experimental studies plates of an active cell are to be observed, further comparisons will only be made for wet plates.

A comparison of a wet charged plate to a wet discharged plate, Figures 24 and 26 respectively, pointed up two significant phenomena. First, the background and the peaks appear to be suppressed in the discharged plate although both x-ray diffraction diagrams were taken using the same scale factors. This has not been checked for repeatability, and possibly it is an operator error, but nevertheless it should be studied further. Additionally, the region of "d" spacings greater than 2.03 show that changes have occurred. This portion of the spectrum will be observed with greater accuracy to determine if more significance can be obtained.

4. Differential Thermal Analysis

The thermograms which can be compared are Figures 33 with 34, and Figure 34 with Figure 36. All of these were run at the same sensitivity; 1 mV/in.

The comparison between two different discharged plates, one with no stand and the other with a 48 stand (Figures 33 and 34) shows a minimum or dip at 517°F for both. The plate without stand seems more endothermic.

When comparing the charged plate, Figure 34, with the discharged plate, Figure 36, it can be seen that the charged plate does not exhibit the minimum at 517°F which the discharged plate exhibits.

The thermograms for the oxide and hydroxide of nickel (Figures 30 and 31) are significant because of their differences.

At this point we can only say that this method of analysis may be useful. New thermocouples are on order to increase the sensitivity and the range of the DTA apparatus. We also plan to run tests in inert and reducing atmospheres as well as the oxidizing atmosphere. This is to bring in any possible pyrolytic reactions and reduction reactions. In air, oxidizing reactions as well as phase transitions, yield significant thermograms.

IV. WORK PLANNED FOR THE SECOND QUARTER

A. ANALYSIS OF X-RAY PATTERNS

The x-rays obtained from sintered plate positives at the end of this quarter will be thoroughly analyzed by comparing peaks to ASTM cards and standards.

B. PREPARATION OF POCKET PLATE CELLS AND TESTING

Thirty pocket plate cells will be prepared and cycled similar to procedures used for sintered plates. Each cell will consist of one pocket or tubular plate wrapped with separator and completely surrounded by a negative plate of excess capacity.

After selection of cells with like capacity and charged storage at 25, 10 and 50°C, these plates will be analyzed by x-ray and chemical means.

C. SPECIAL TESTS TO DETERMINE DIFFERENT EFFECT ON POSITIVE PLATE CHARACTERISTICS BETWEEN SEALED AND VENTED CHARGE

The experimental handling of a large number of cells is much simpler as vented cells than as sealed cells. In order to justify such a procedure, some past experimental findings are required in addition to a specific test.

The usual differences between sealed and vented nickel-cadmium cells lies in the suppression of hydrogen from the negative electrode, and in a decrease of the amount of electrolyte. As a consequence of sealing a third difference arises; that is a vented cell anode is overcharged at constant pressure while the sealed cell anode is overcharged at an increasing pressure.

The hydrogen suppression is dependent upon the cathode, and so requires no further attention.

The increasing pressure during sealed cell charge affects the potential of the anode. At the end-of-charge, the potential determining anode process is that of an oxygen producing electrode. The potential of such an electrode is dependent upon pressure. Thus the anode in a sealed cell does become more anodic as oxygen pressure increases. (See Power Sources Conf. 1962, Seiger et alia).

A good test for the similarity of compounds appears, then, to be based on the number of coulombs that may be passed through an anode during charge before the pressure step is encountered. This should be done in "vented" and "sealed" conditions. The vented condition will be a flooded cell. The sealed condition will be a cell with no excess electrolyte. The latter will be done first. A sealed cell with a pressure transducer will be prepared. The cell will be evacuated and then charged. The point at which the pressure starts to rise will be determined. The cell will then be flooded and air admitted. The cell will then be closed off. The plates then will be in a set of experimental conditions at the time of initial pressure rise that will be completely equivalent to vented cells. The number of coulombs passed in these two cases will then be evidence for the formation of identical or different compounds. The assumption being that an identity of coulombs to charge the nickel hydroxide means an identity of compounds.

D. THE EFFECTS OF SEVERAL ATMOSPHERES ON D.T.A. STUDIES

Differential thermal analysis will be made with plate material and standards under inert oxidizing and reducing atmospheres.

E. SHELF LIFE TESTS FOR SINTERED PLATE POSITIVES WILL CONTINUE

F. WORK ON FAST DECAY OXIDE STUDIES - PHASE II - WILL BEGIN

The schedule is moving along at about the rate set in the work plan of the First Monthly Status Letter.

V. MAN HOURS

TITLE	HOURS
PROJECT DIRECTOR	235
STAFF SCIENTIST	653
JUNIOR ENGINEER	544
TOTAL	1432

DOLLAR EXPENDITURES

MATERIAL	LABOR	TOTAL COST
$232.	$5510.	$12,048.

COMMITMENTS DURING REPORT PERIOD

UNIT	ITEM	COST
ASSORTED	ELECTRONIC EQUIPMENT	$95.

APPENDIX I.

MIXED SOLUTION ELECTRODES

Because of the shift of X-ray lines, it had been suggested that $Ni(OH)_2$ and NiOOH form mixed solutions. This can be tested by investigating the slope of the Nernst equation.

Consider the reaction:

$$(1)\quad NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$$

The Nernst equation is given by:

$$(2)\quad E = E^o - 0.06 \log \frac{[NiOOH]\ {}^aH_2O}{[Ni(OH)_2]\ {}^aOH^-}$$

Since the concentration of electrode is not altered much by the state-of-charge, one may write

$$(3)\quad E = E^{o^1} - 0.06 \log \frac{[NiOOH]}{[Ni(OH)_2]}$$

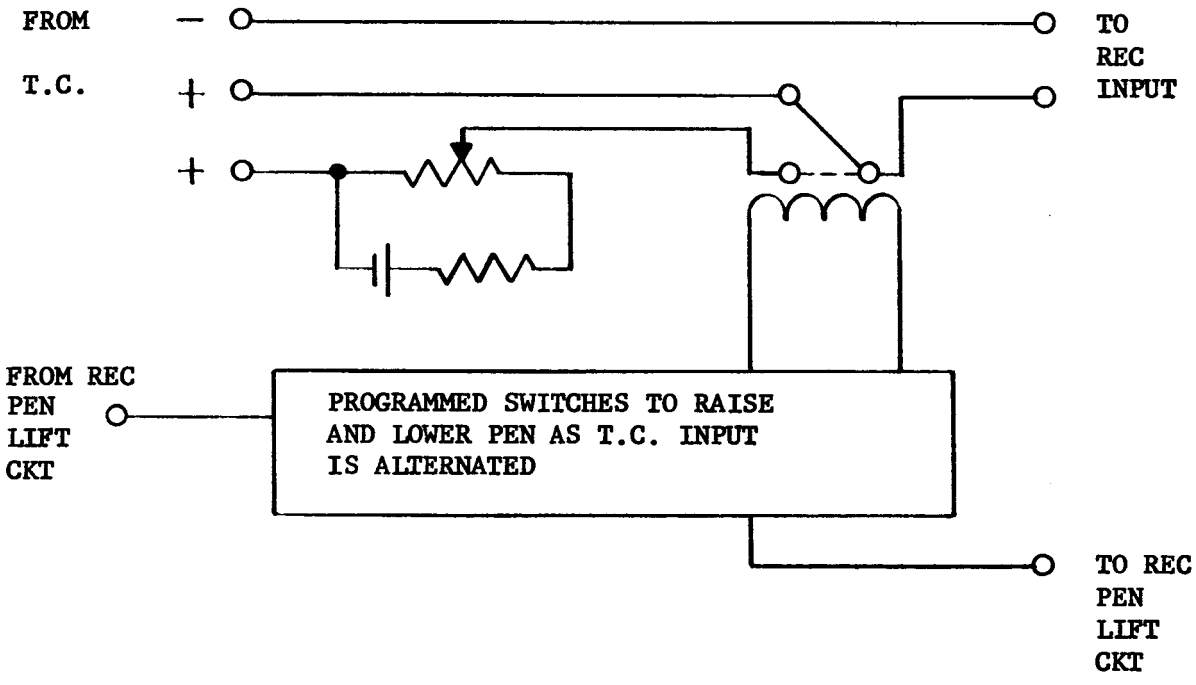
The concentrations are stated as mole fraction. Let N = mole fraction of $Ni(OH)_2$ and N_o = mole fraction of NiOOH. Since $N_o + N_r = 1$, equation (3) becomes:

$$(4)\quad E = E^{o^1} - 0.006 \log \frac{1-Nr}{N_r}$$

The equation can hold only when an electrode is poised in the sense that the argument of the logarithm does not approach zero nor infinity. Hence, the change of open circuit potential of a positive electrode may be determined at, say, 50% charged and 10% charged. N_r is 0.5 and 0.9 respectively for these conditions. The change of potential between these points is calculated to be 57 mV. Such a change is additional evidence for a solid solution.

In a recent paper Conway and Gileadi (Electrochem. Society Meeting, Boston, 1962) were able to show that over a range of oxidation from 20% to 50% charged, the nickel oxide exhibits a constant reversible potential. Up to 10% charged, there is, perhaps, a surface phase that is being charged. Alternatively, the β NiOOH may have reached its limit of solubility in $Ni(OH)_2$.

The fact that Conway and Gileadi's careful measurements show a constancy over 10% to 50% state-of-charge implies that at least for the major part, that β NiOOH is insoluble in $Ni(OH)_2$. The calculated change between these points is 57mV and the measurements were made to one-tenth of a millivolt. No doubt exists as to the conclusion.



MECHANICAL SWITCH FOR X-Y RECORDER

TABLE I

CYCLING DATA

CELL NO.	TIME TO 0 VOLTS PRELIMINARY CYCLE 1	TIME TO 0 VOLTS PRELIMINARY CYCLE 2	TIME TO KNEE OF FIRST PLATEAU 6TH CONSTANT LOAD CYCLE	
1	164	142	150	M
2	190	146	185	
3	175	145	150	M
4	170	157	150	M
5	182	160	147	M
6	164	110	70	
7	161	150	70	
8	175	161		
9	175	157	165	H
10	175	161	147	M
11	162	95	142	L
12	165	153	130	
13	178	157	155	H
14	120	95	154	H
15	162	130	147	M
16	170	159	138	L
17	160	152	135	L
18	165	155	70	
19	165	144	85	
20	155	141	145	L
21	170	148	152	H
22	170	148	150	M
23	160	144	182	
24	168	148	152	H
25	160	142	138	L
26	160	142	180	
27	155	143	140	L
28	155	143	157	H
29	165	141	150	H
30	170	144	138	L

TABLE II

X-RAY "D" SPACINGS

SINTERED NICKEL	Ni(OH)	POLYETHYLENE	SINTERED Ni IN POLYETH.	CHARGED PLATE WET IN POLYETH.	CHARGED PLATE DRY	DISCHARGED PLATE WET	DISCHARGED PLATE DRY
2.03	4.56		4.12	4.16	6.95	4.36	6.69
1.76	3.76		2.48	2.47	3.50	4.12	6.49
1.246	3.71	4.12	2.03	2.03	2.38	2.47	4.51
1.242	3.02	2.42	1.76	1.76	2.02	2.03	4.12
1.061	2.69		1.24	1.24	1.75	1.76	3.50
1.051	2.34		1.06	1.06	1.24	1.24	3.43
	2.03		1.01		1.06	1.060	3.37
	1.94				1.01		2.64
	1.75						2.31
	1.56						2.00
	1.48						1.74
	1.33						1.54
	1.29						1.52
	1.28						1.40
							1.23
							1.053
							1.008

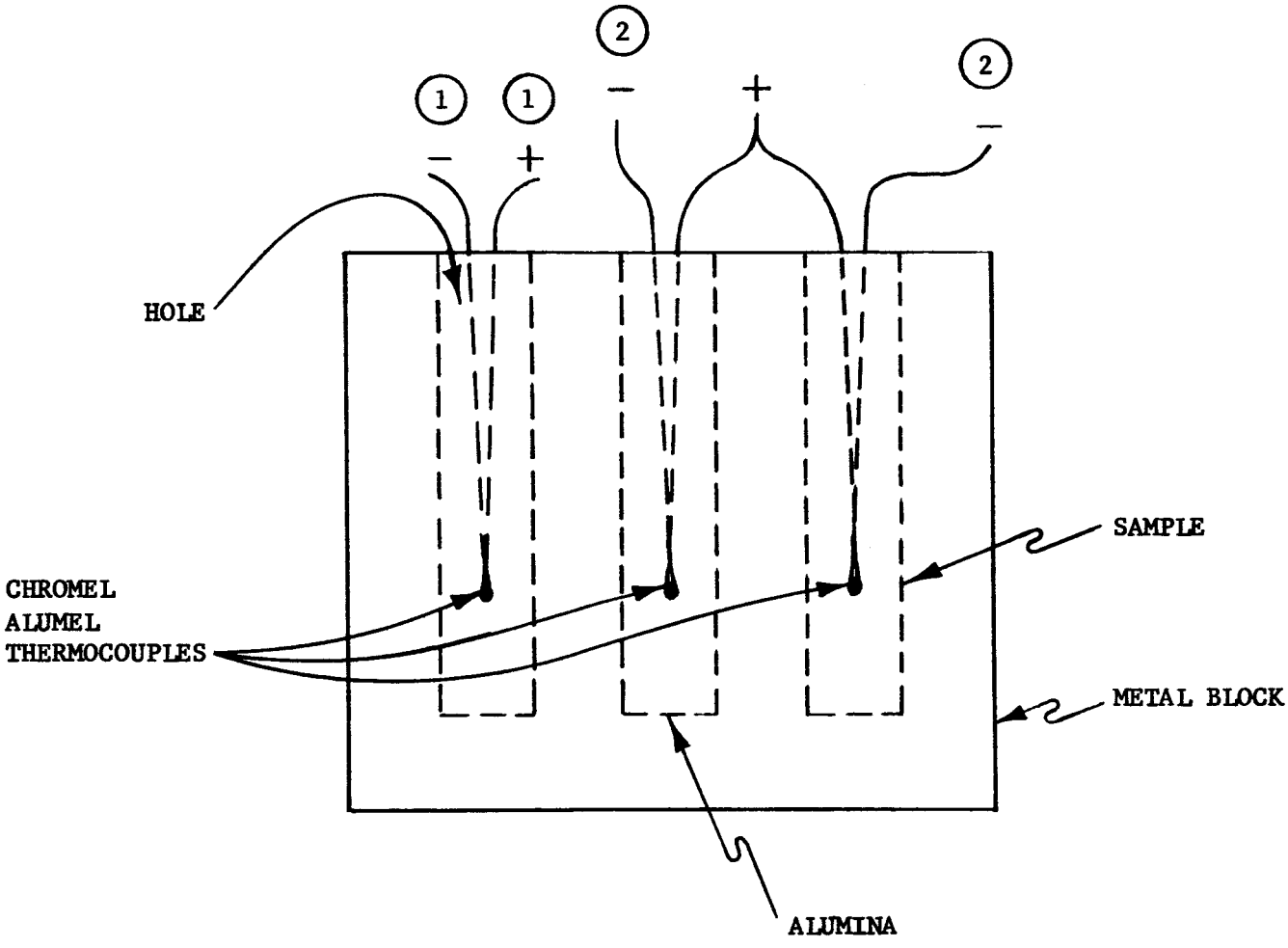


FIG. 1 - D.T.A. HEATING BLOCK
1-1 To Abscissa of the X-Y Recorder
2-2 To Ordinate of the X-Y Recorder

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METUCHEN, N. J.

M2646
AB8400

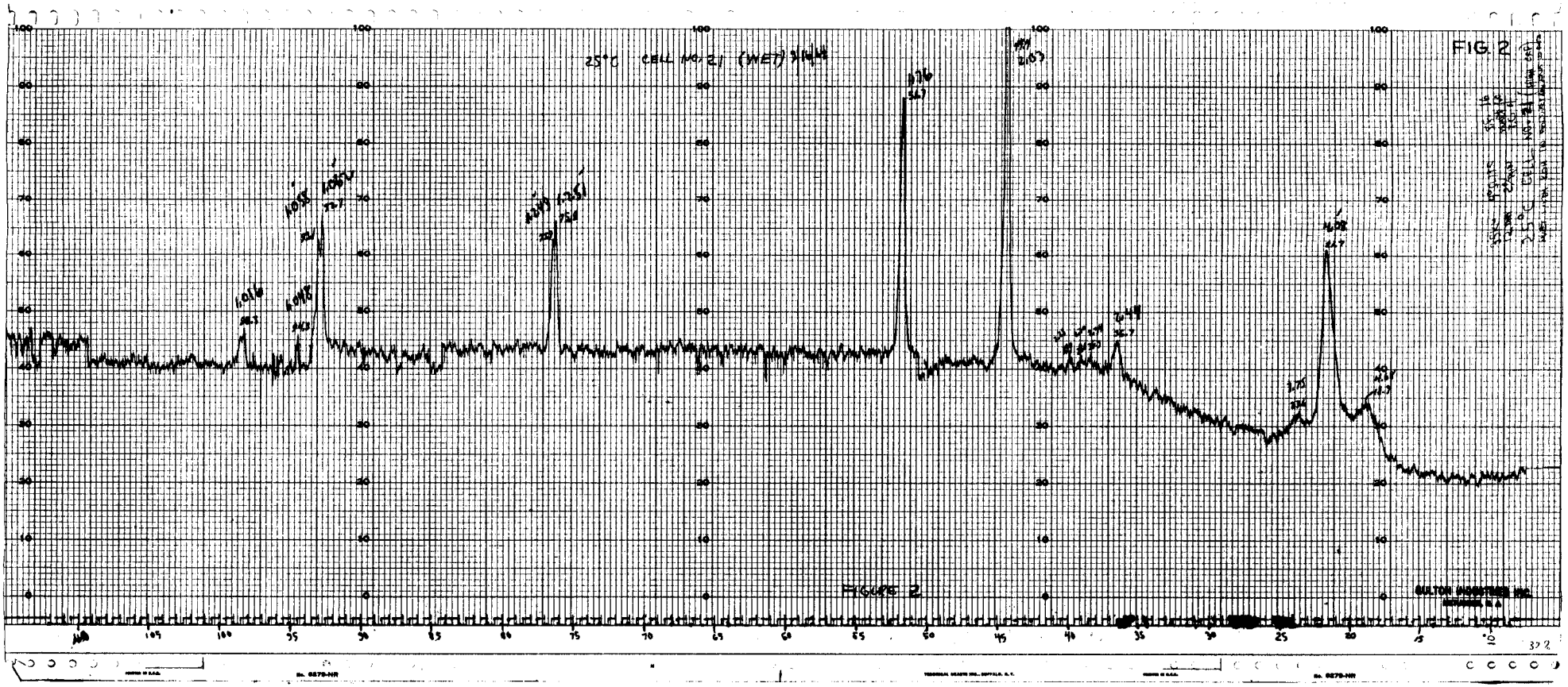


FIG 2

FIGURE 2

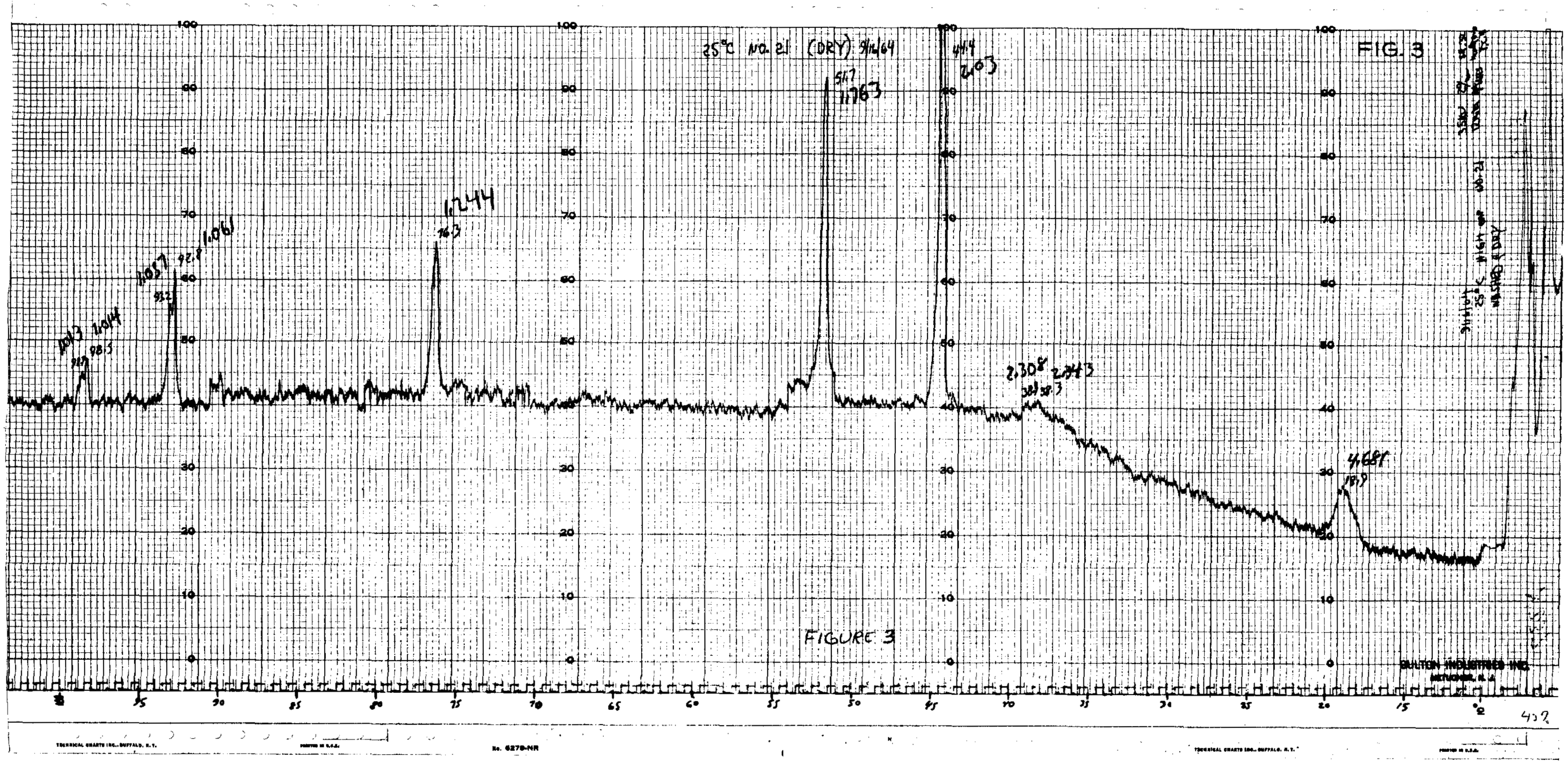
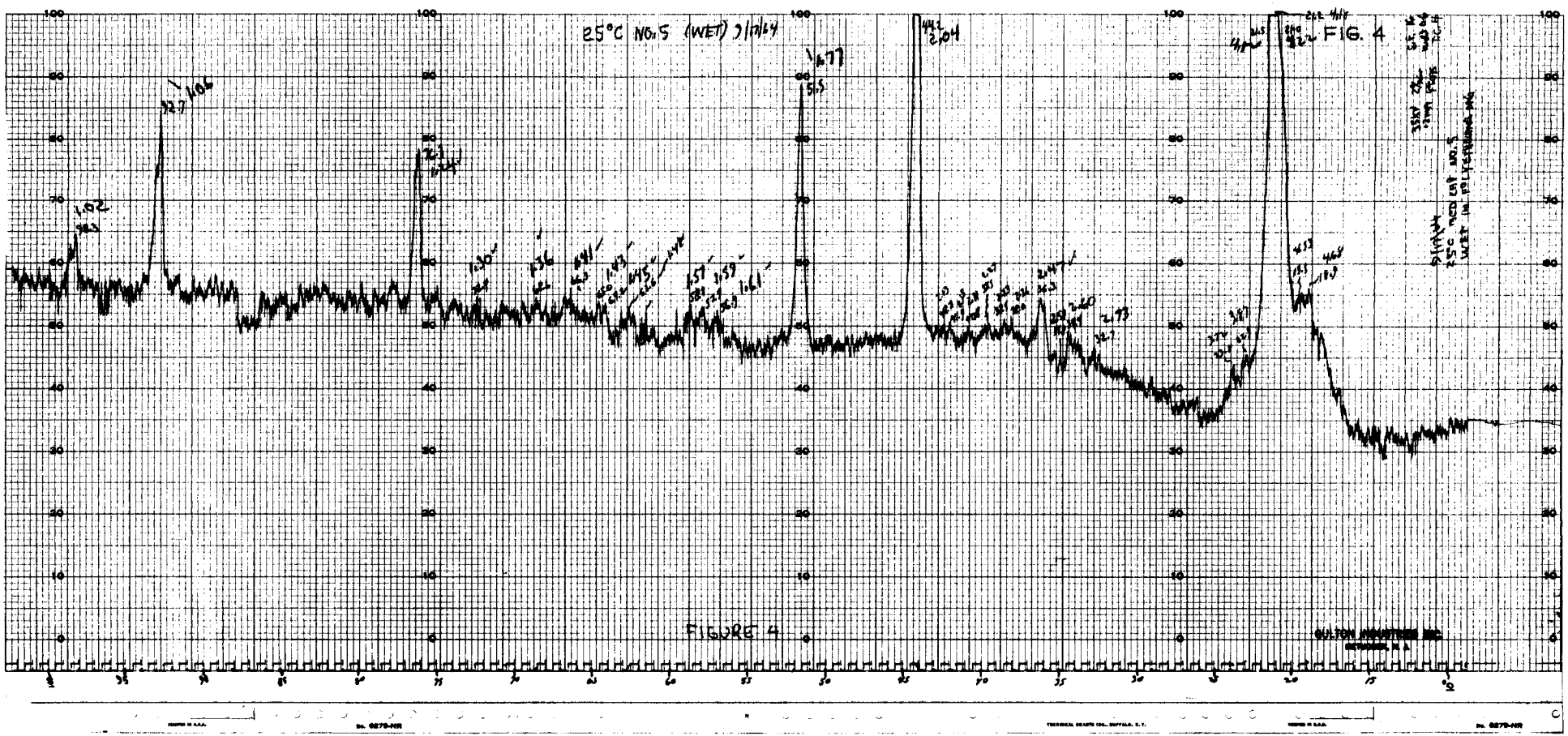
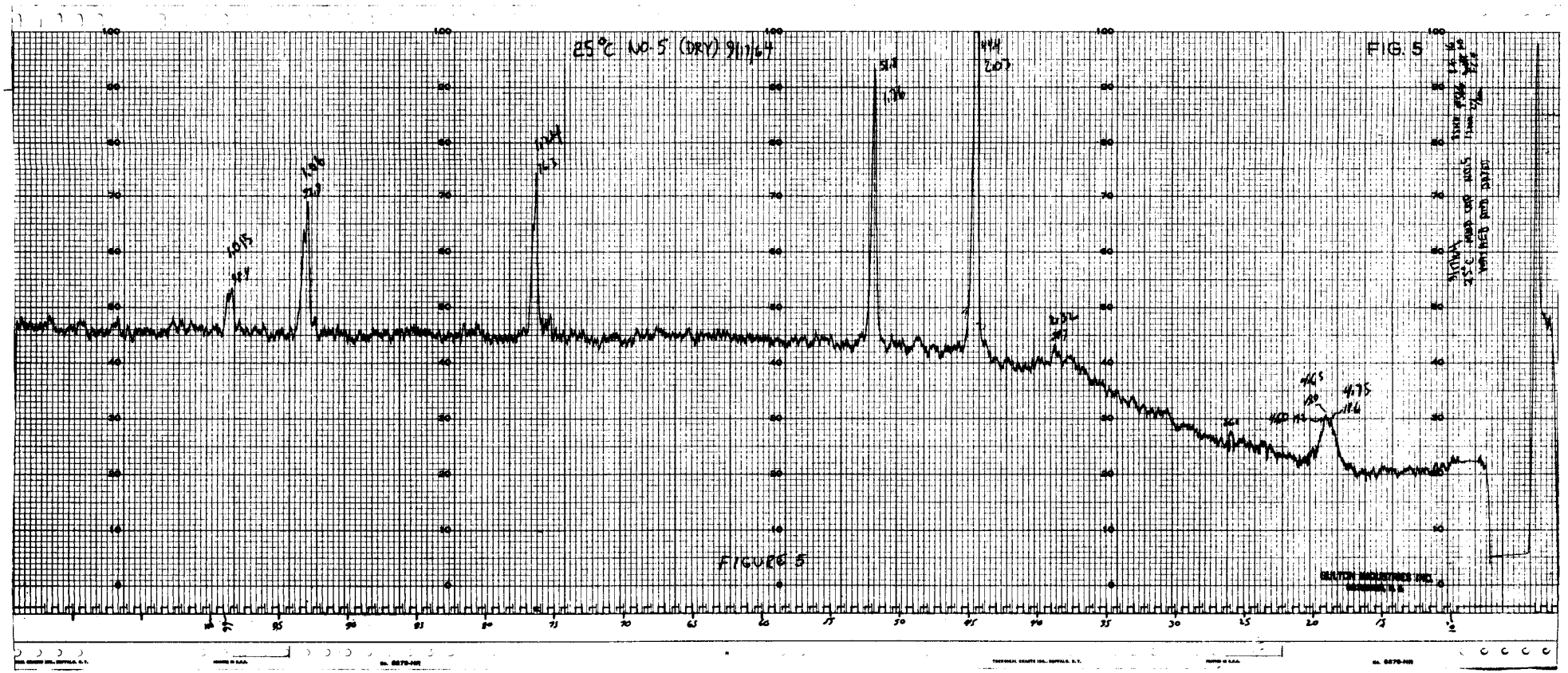
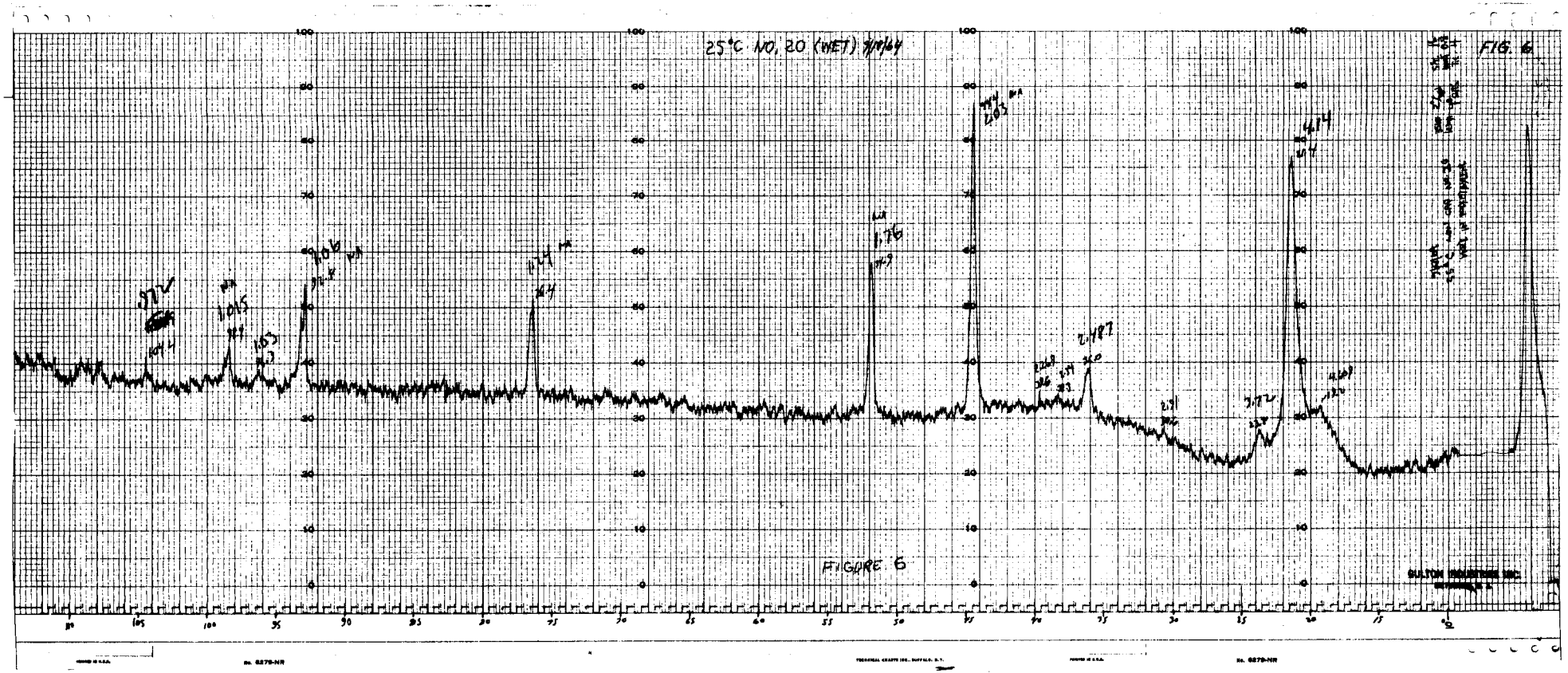
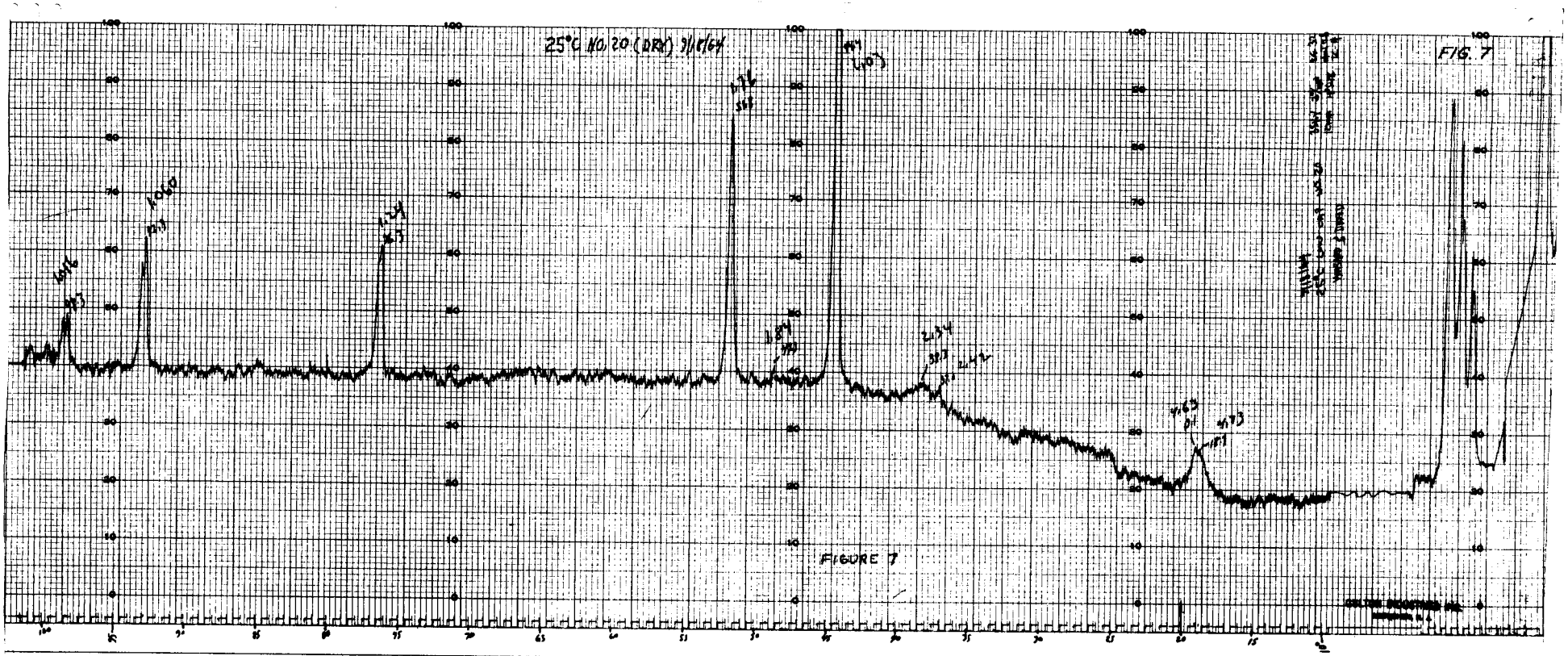


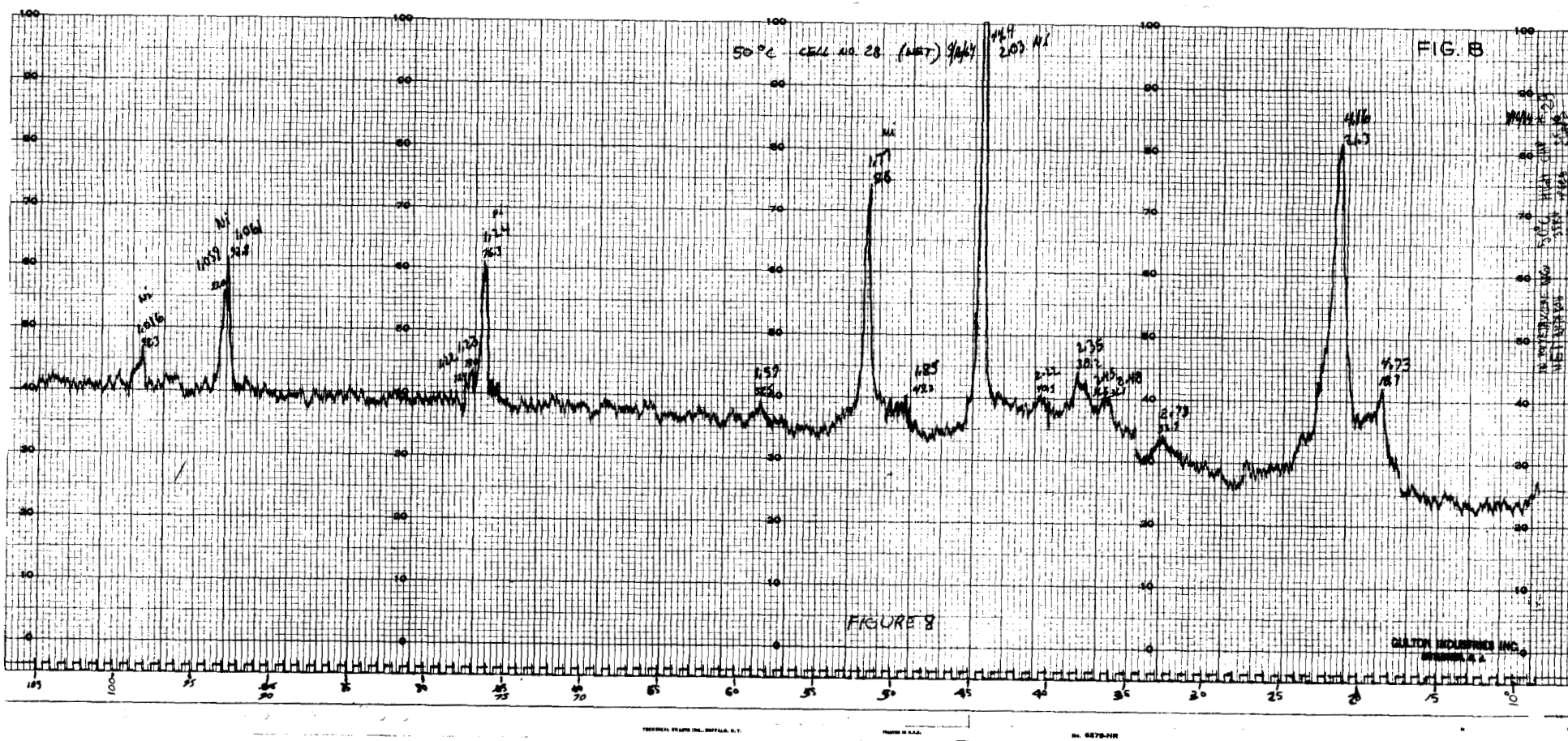
FIG. 3
25°C NO. 21 (DRY) 9/16/64
1.1763
2.03
1.244
1.061
1.087
4.681
2.308
2.343
FIGURE 3


25°C NO. 5 (WET) 3/17/64
FIG. 4
FIGURE 4
FULTON INDUSTRIES INC.


25°C NO. 5 (DRY) 9/17/64
FIG. 5
FIGURE 5


25°C N0, 20 (WET) 3/10/64
FIG. 6
FIGURE 6


25°C NO. 20 (DRY) 9/18/64
FIG. 7
FIGURE 7


50°C cell no. 28 (wet) 9/4/64
FIG. B
FIGURE 8
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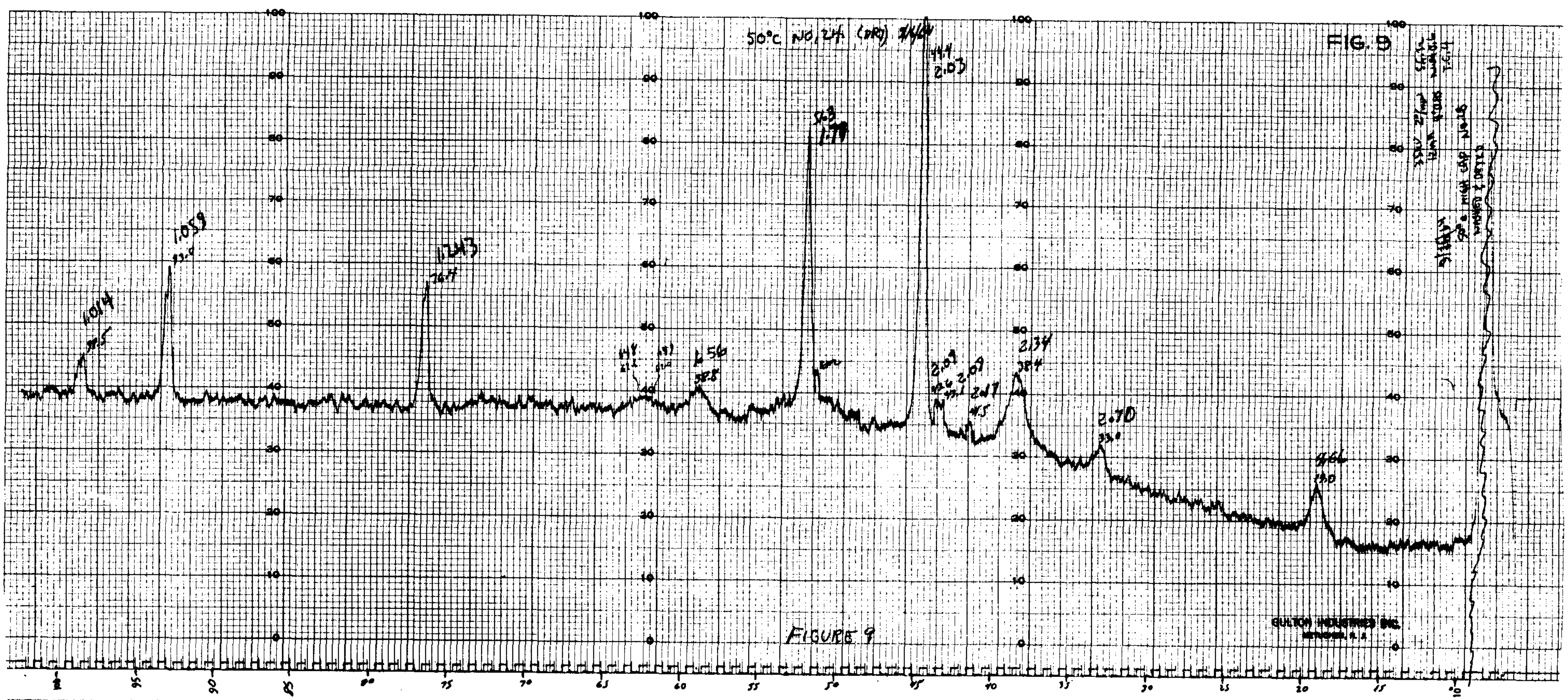
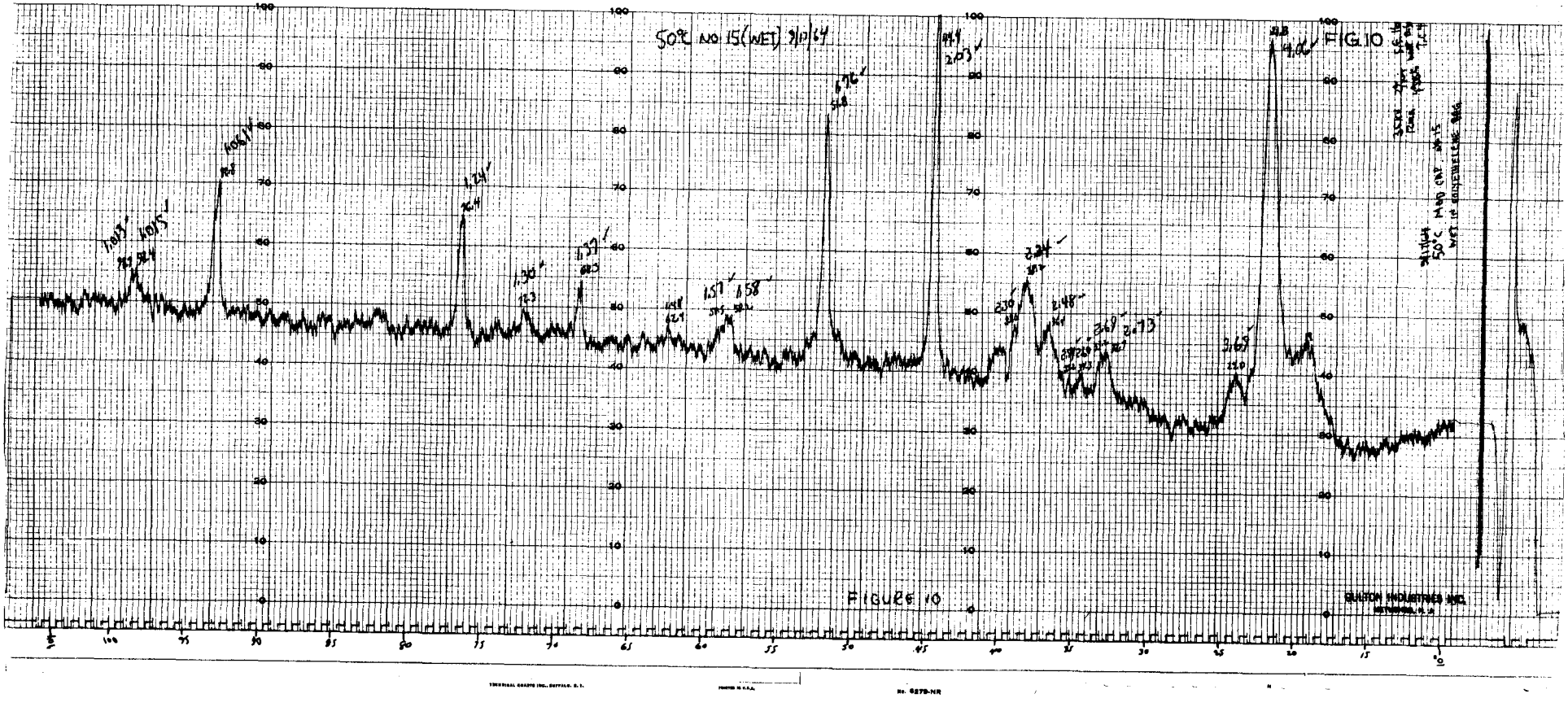
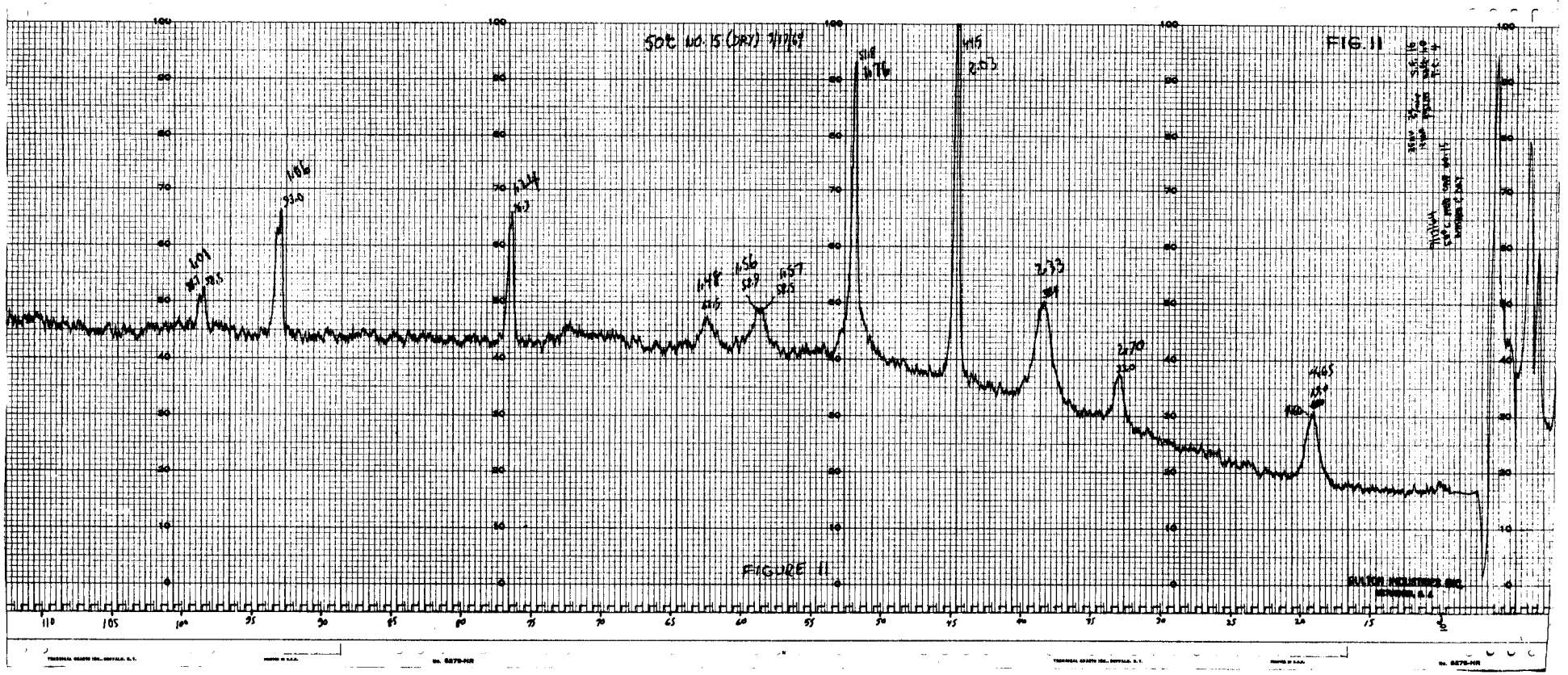
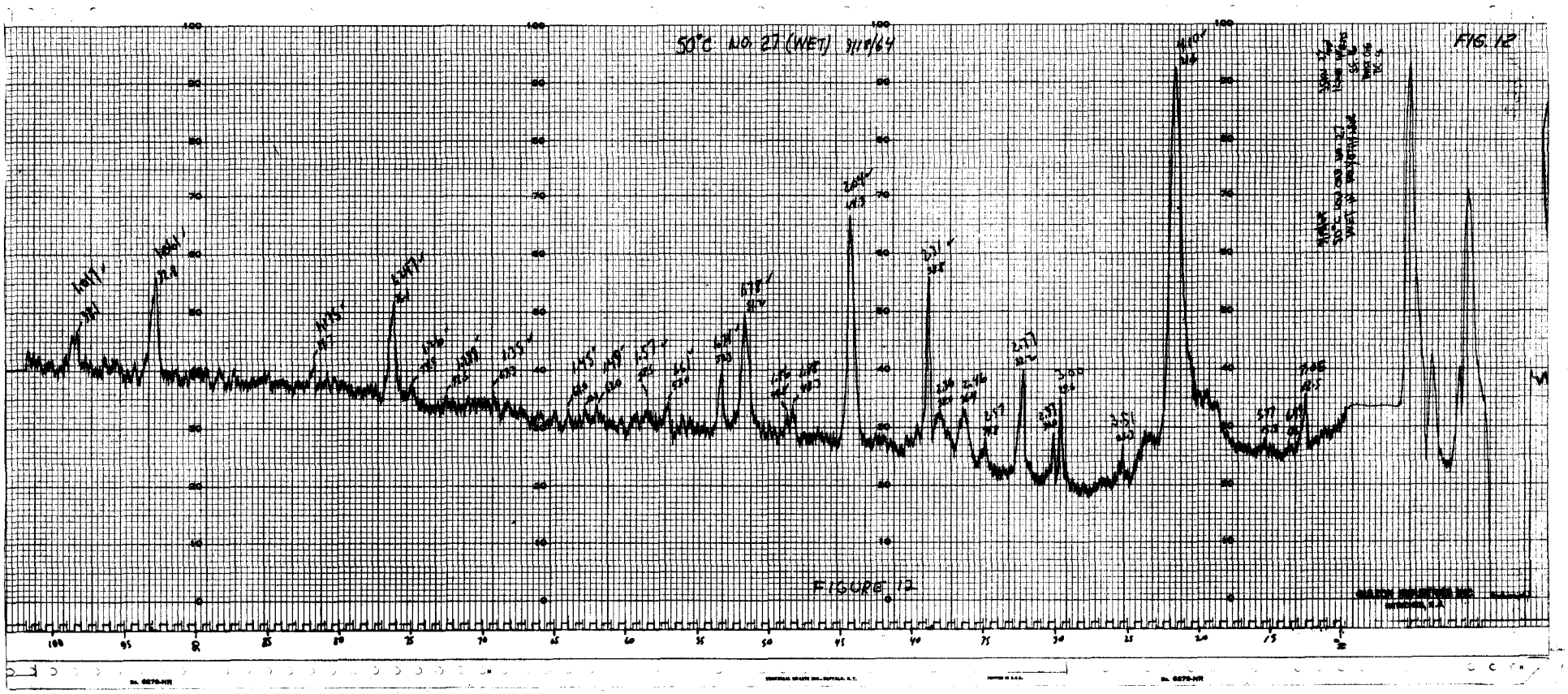
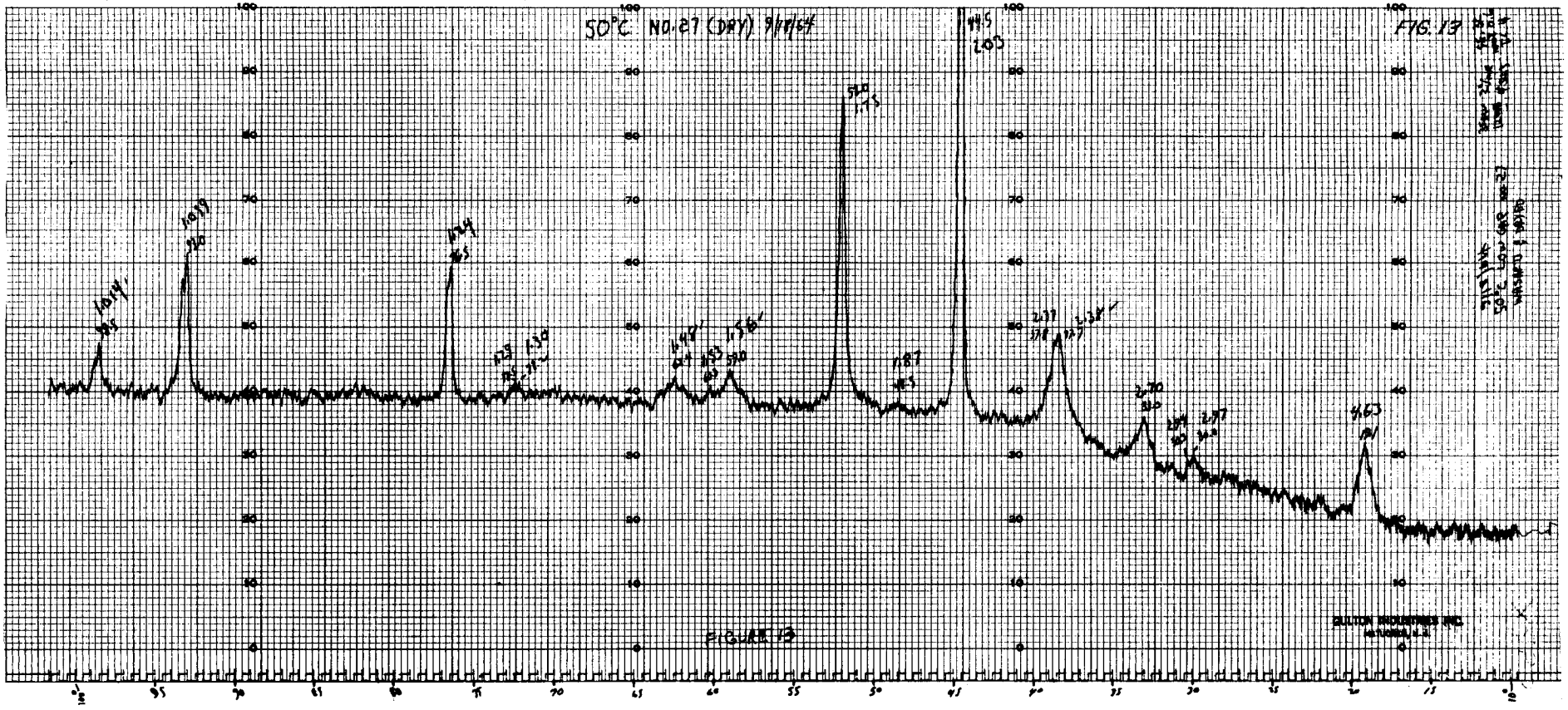


FIGURE 9


50% NO 15 (WET) 9/10/64
FIG 10
FIGURE 10


Sat no. 15 (DRY)
FIG. 11
FIGURE 11


50°C NO. 27 (WET) 3/18/64
FIG. 12
FIGURE 12.


50°C. NO. 27 (DRY) 9/11/54
FIG. 13
FIGURE 13
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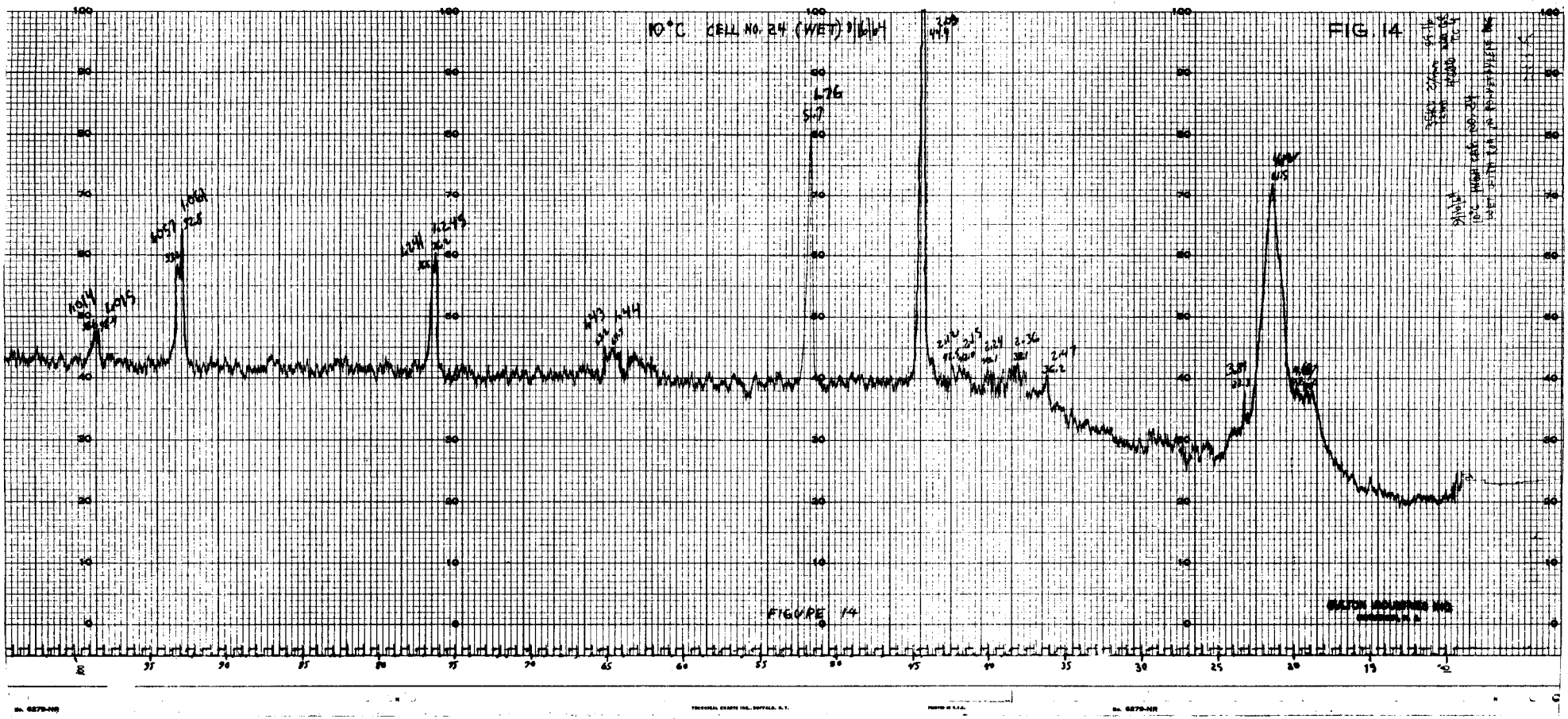
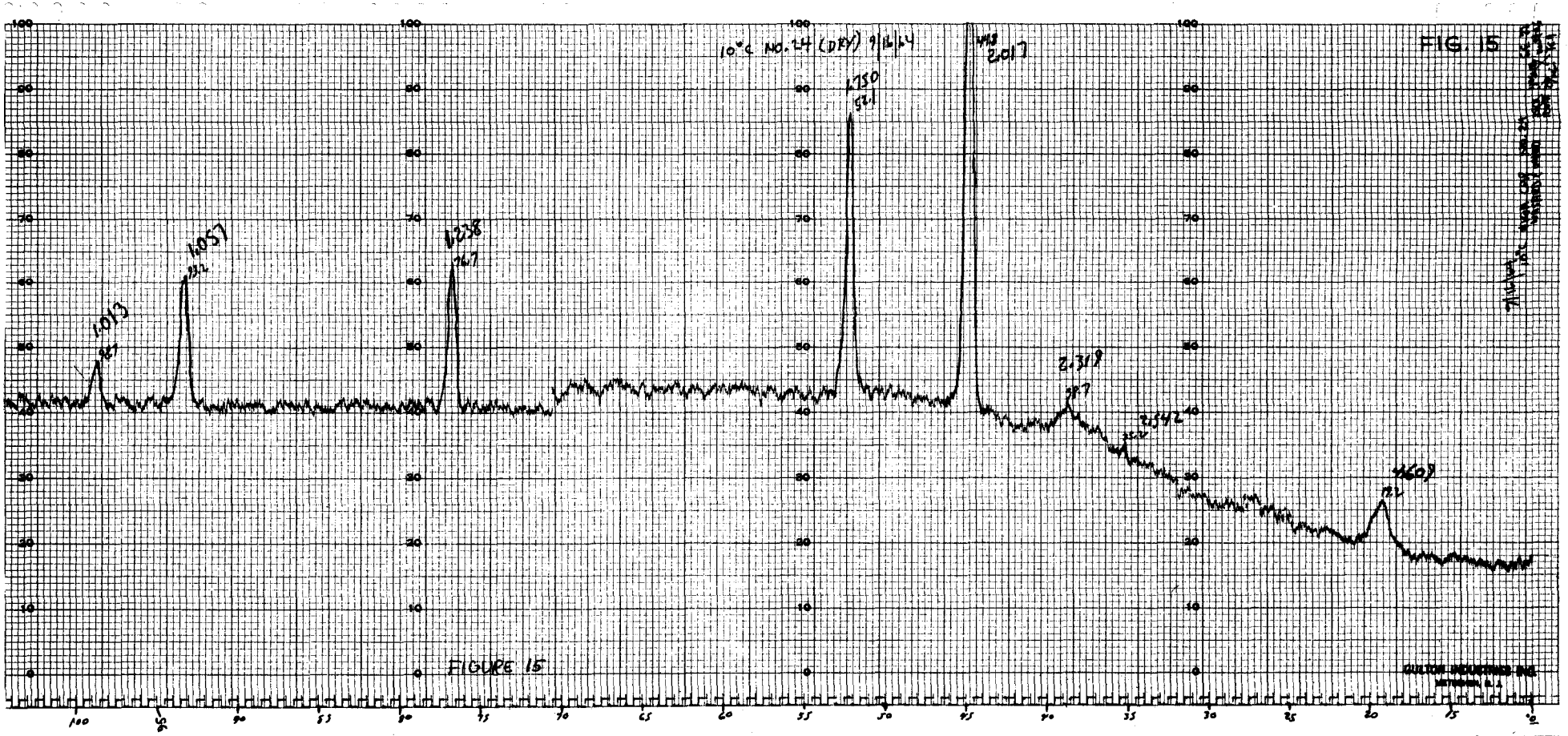
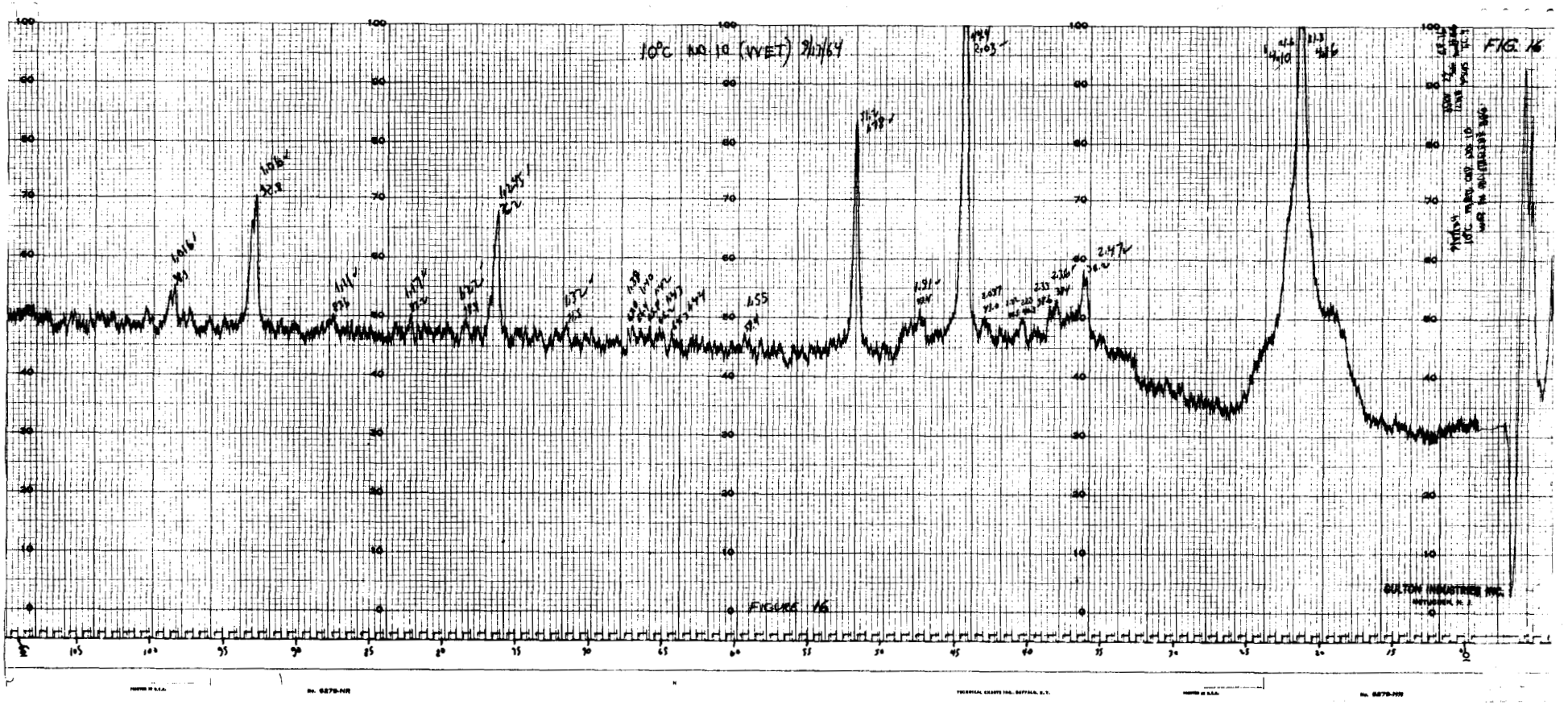
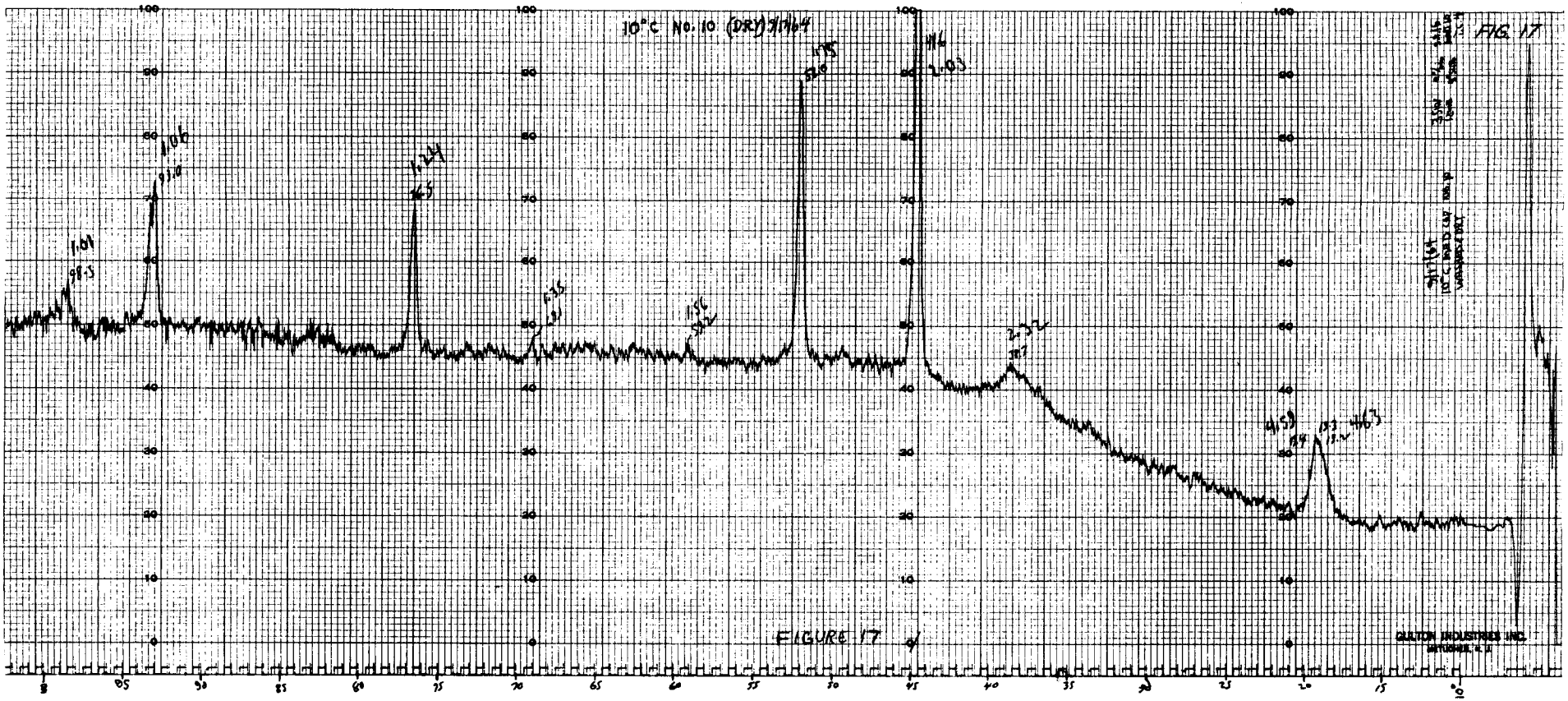
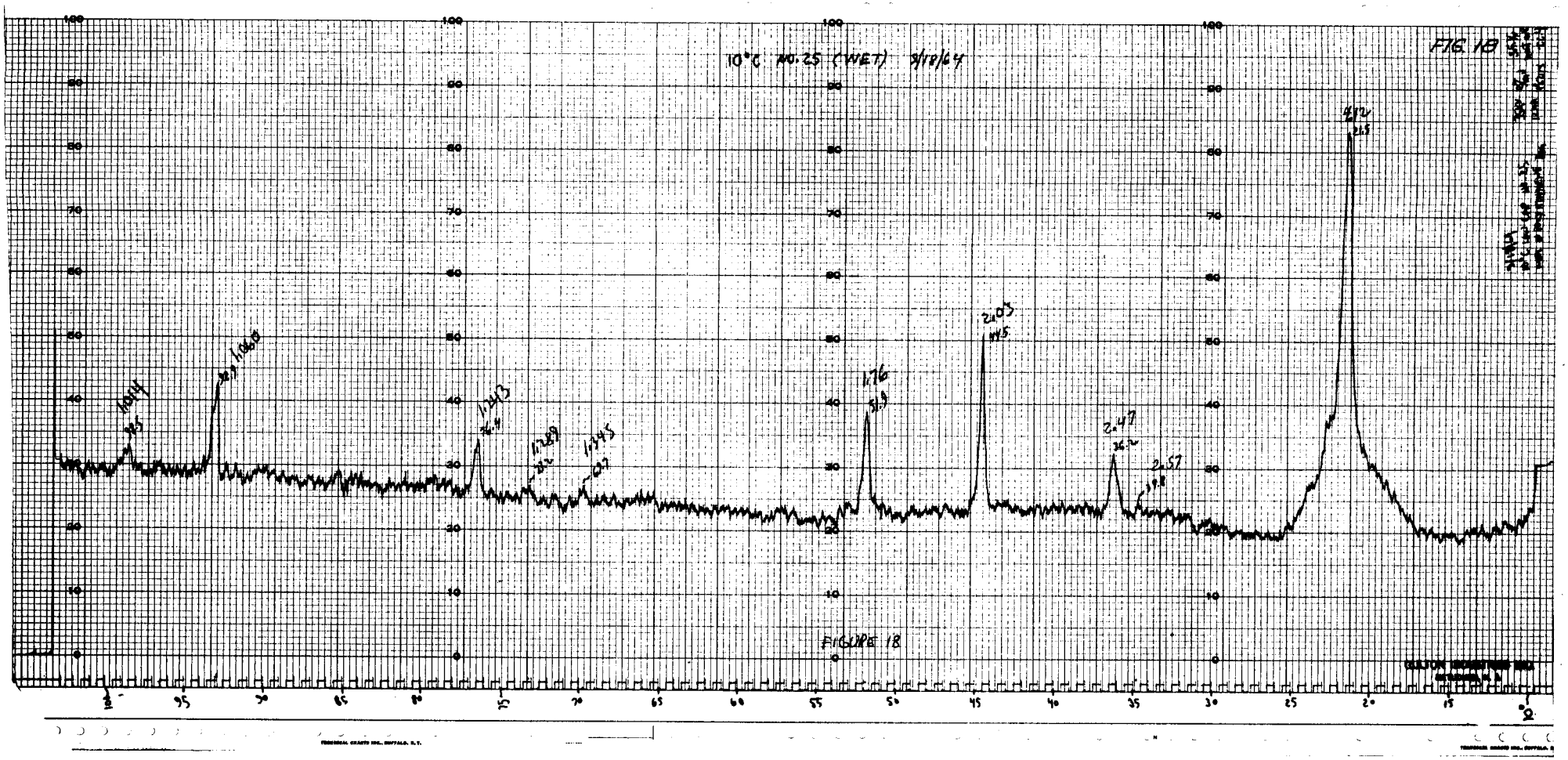

10°C CELL NO. 24 (WET)
FIG. 14
FIGURE 14

FIG. 15


10°C NO. 24 (DRY) 9/6/24
1.013
98.1
1.057
132
1.238
76.7
1.750
52.1
2.017
2.319
28.7
2.542
2.602
72
FIGURE 15


10°C NO 10 (WET) 9/17/64
FIG. 16
FIGURE 16
GULTON INDUSTRIES INC.


10°C No. 10 (DRY)
FIG. 17
FIGURE 17
GULTON INDUSTRIES INC.


10°C NO. 25 (WET) 3/18/64
FIG 18
1.094
1.068
1.243
1.289
1.345
1.76
2.057
2.47
2.57
4.72
FIGURE 18

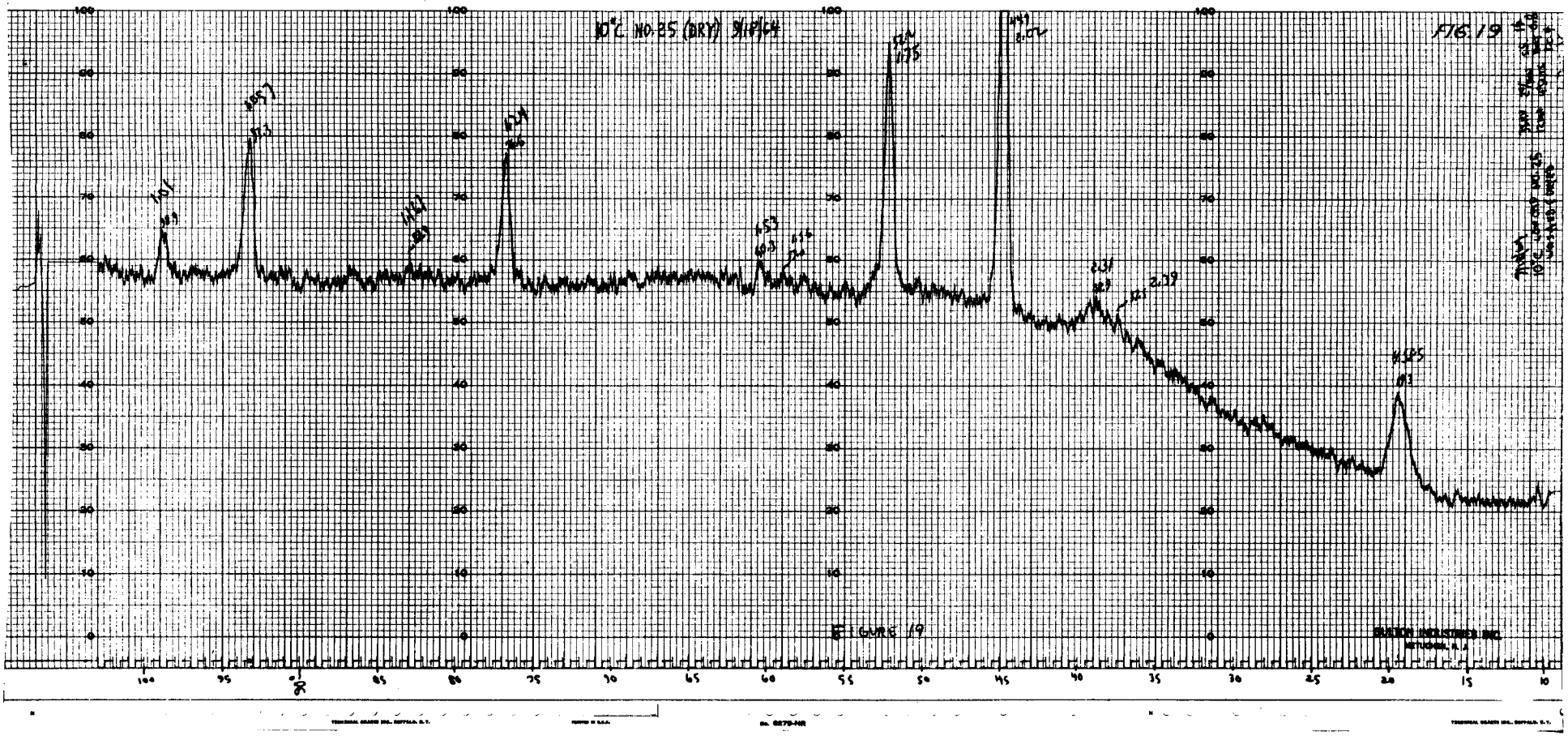

10°C NO. 25 (DRY) 3/18/64
FIG. 19
FIGURE 19

FIG. 20A

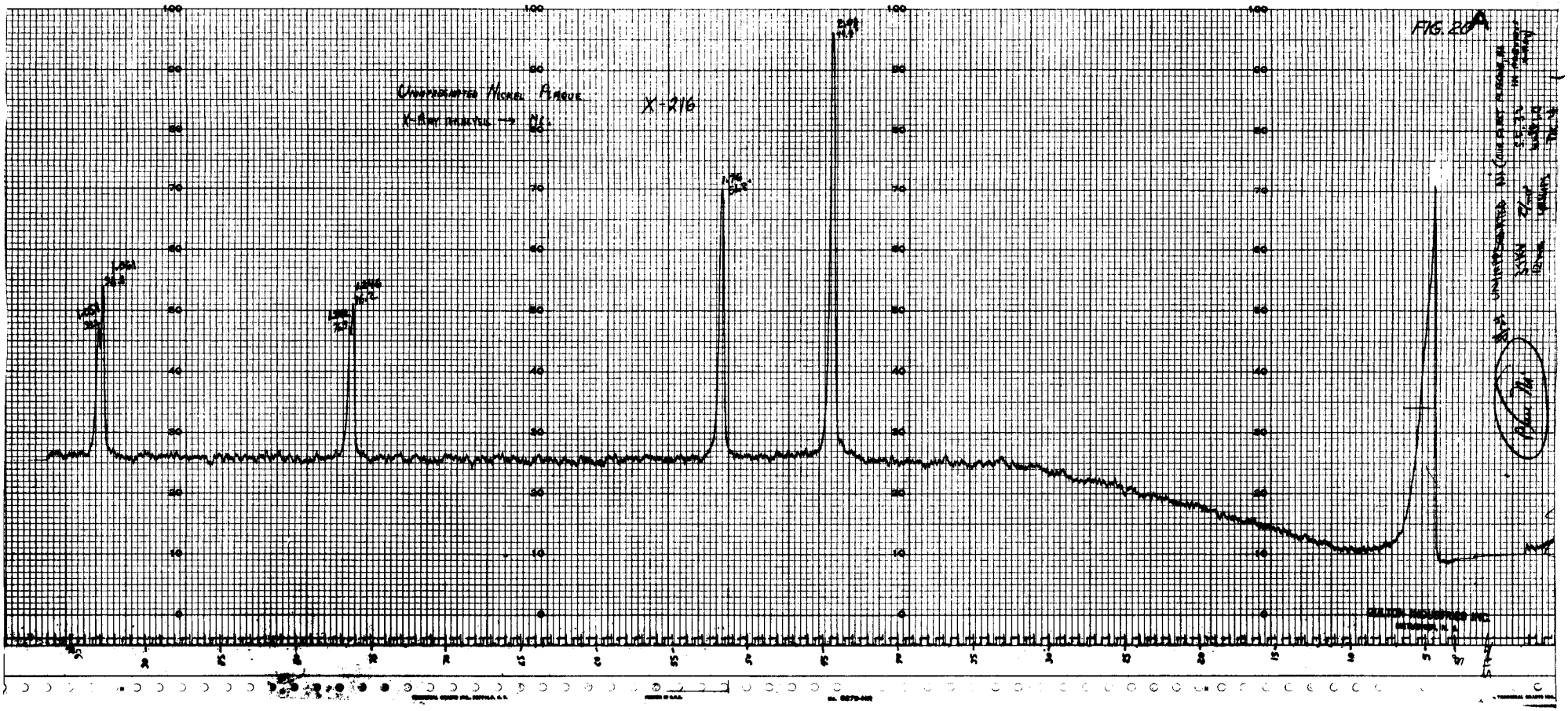
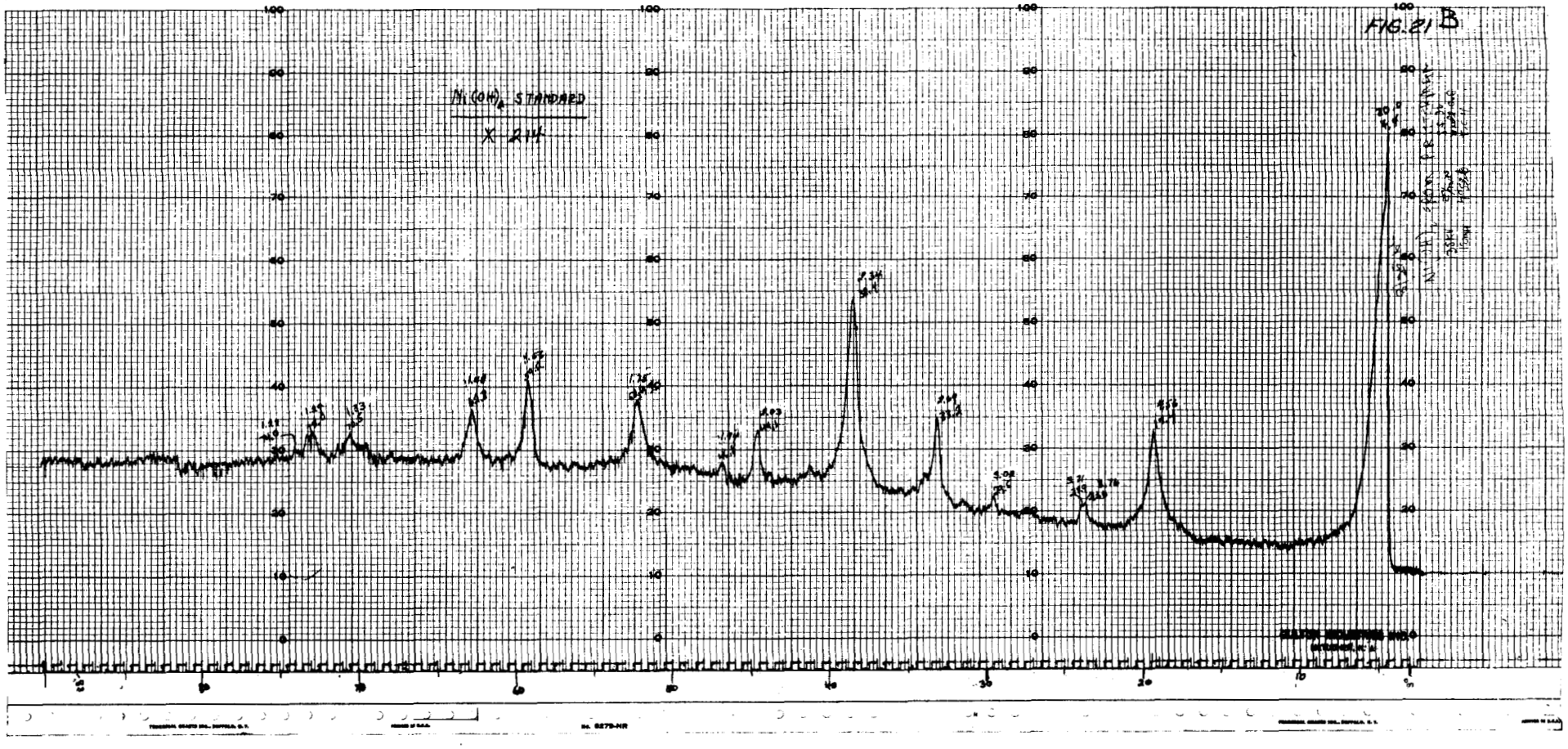


FIG. 21 B



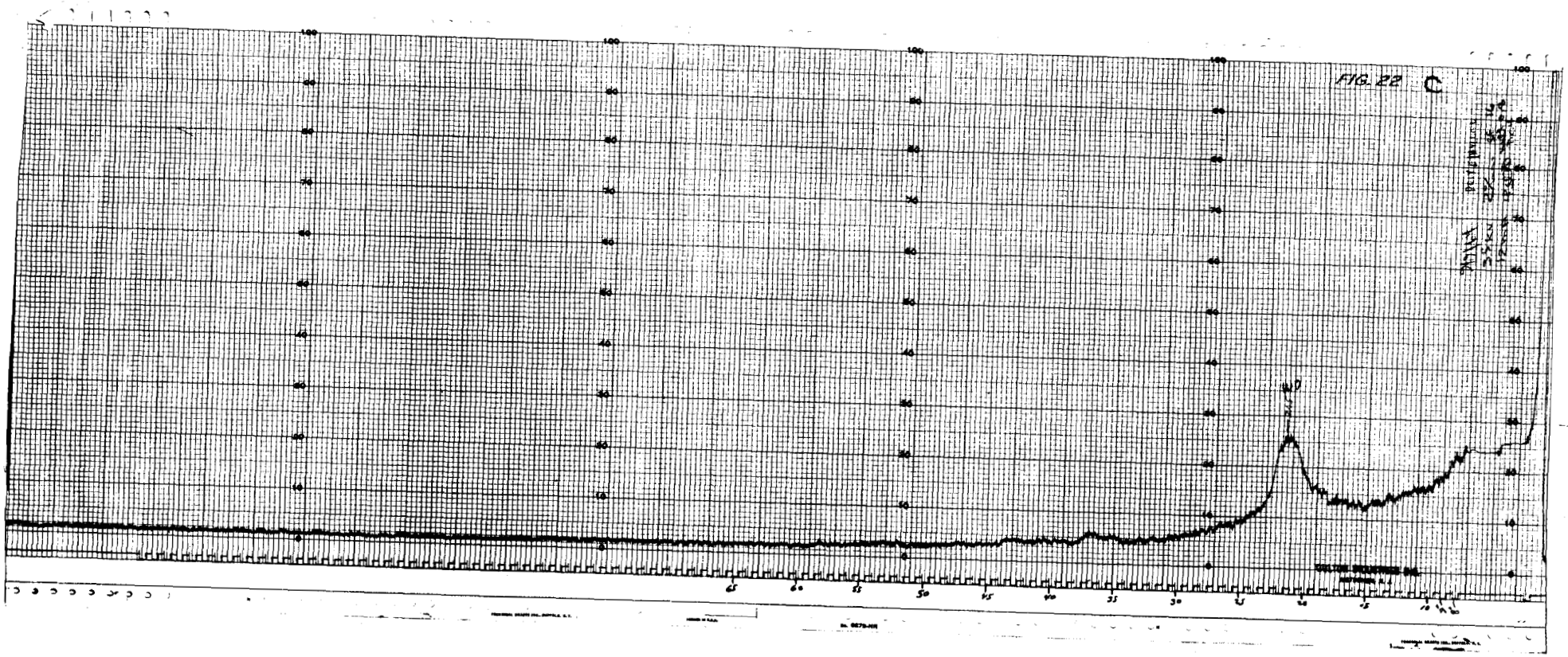


FIG. 22 C

Fig. 8

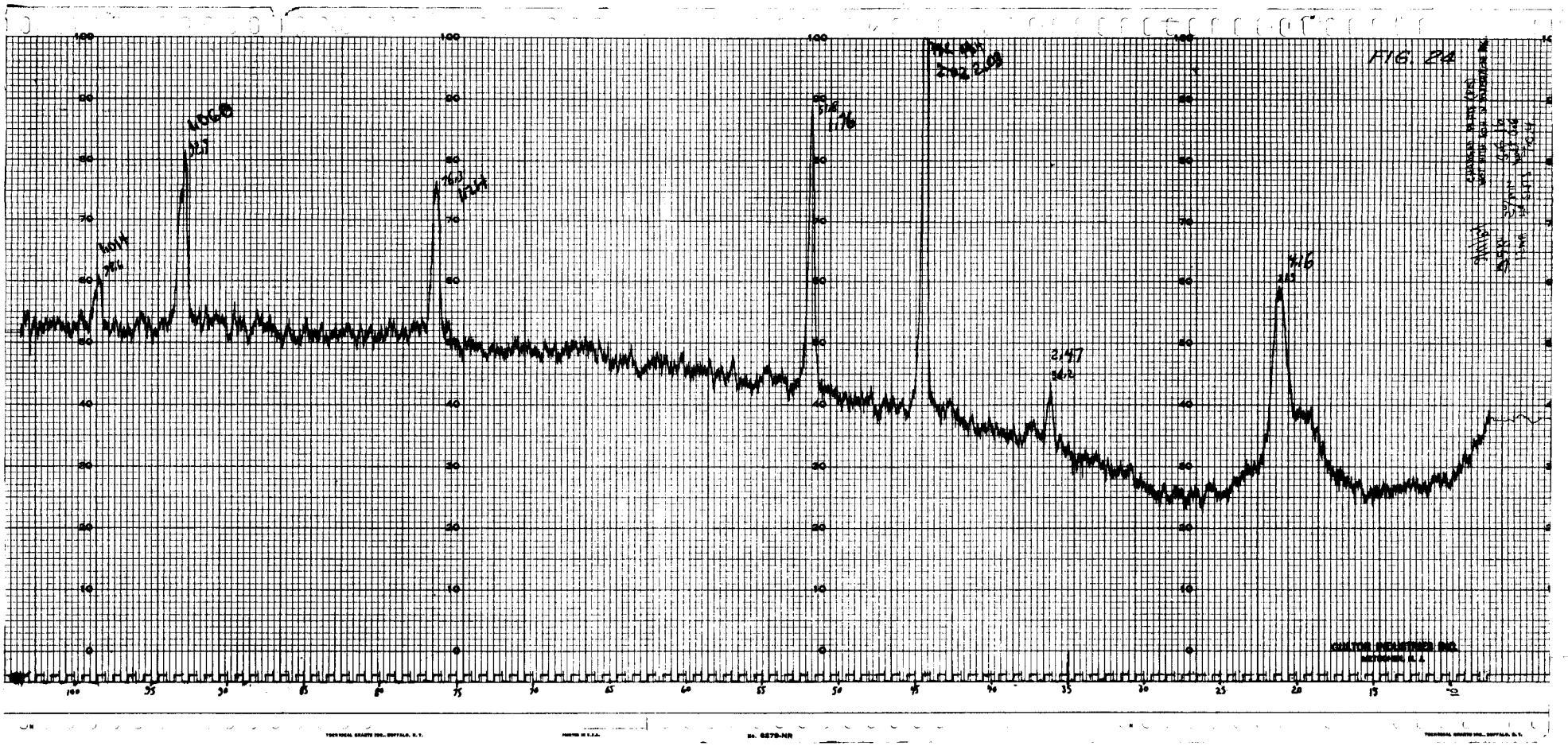


FIG. 24
2.147
#16

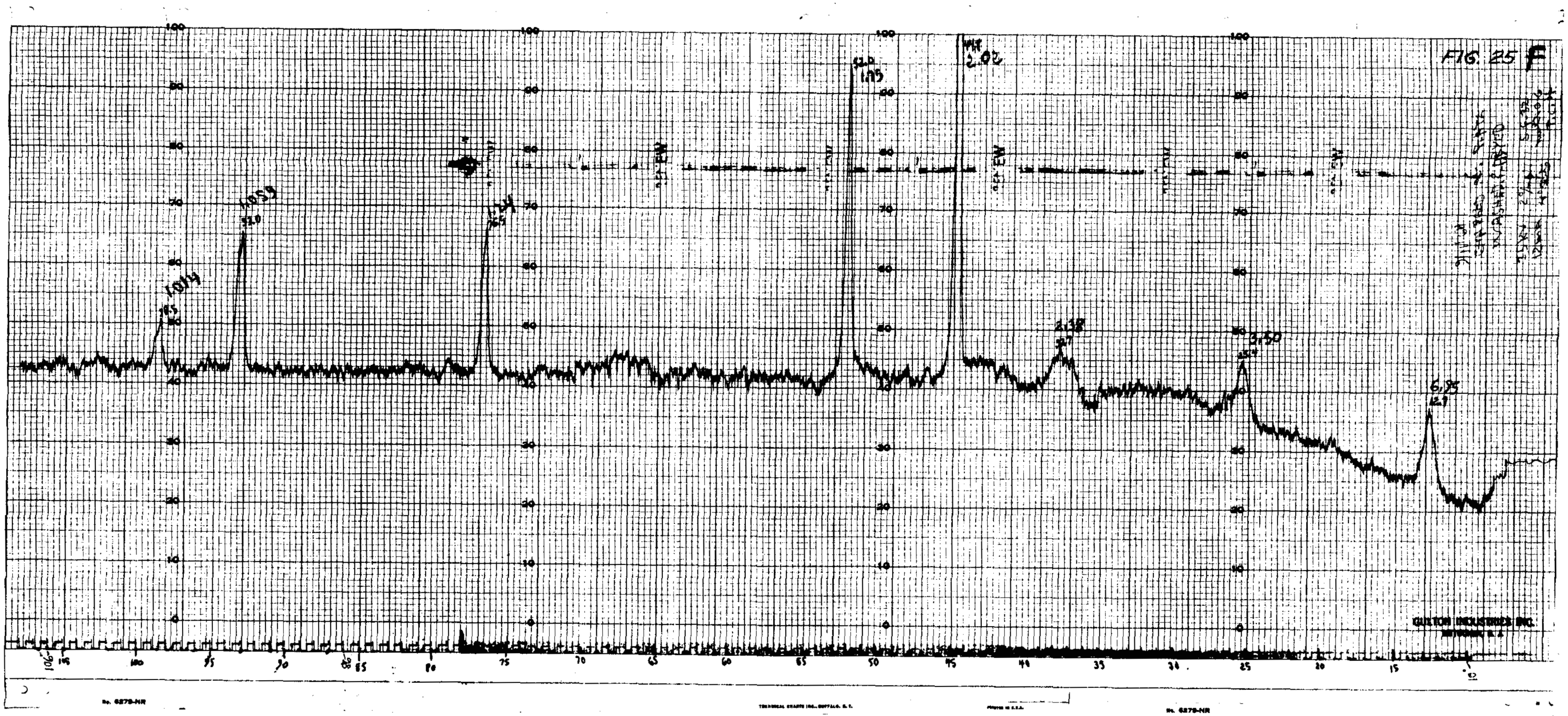
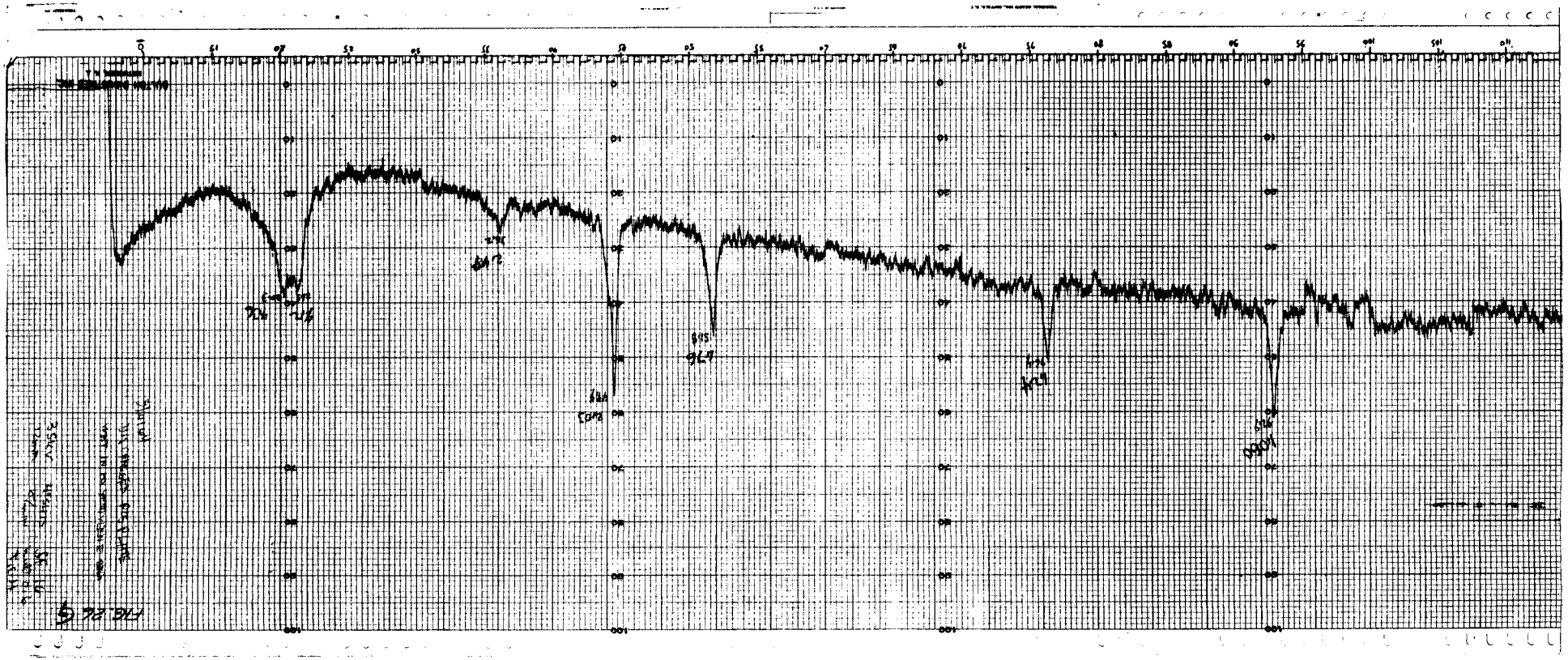


FIG. 25 F
2.02
1.15
1.24
1059
1014
2.38
3.50
6.85
GULTON INDUSTRIES INC.
No. 6275-NR



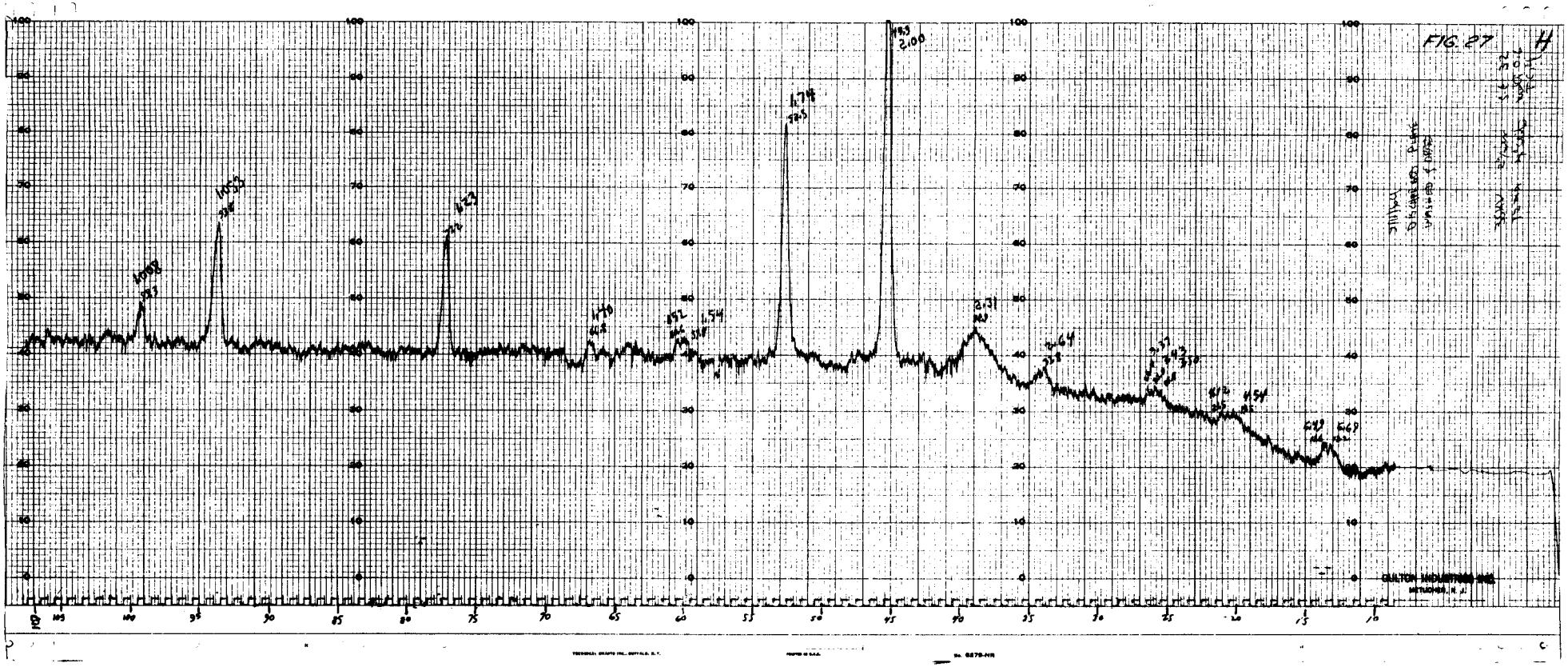


FIG 27 H
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FIG. 28

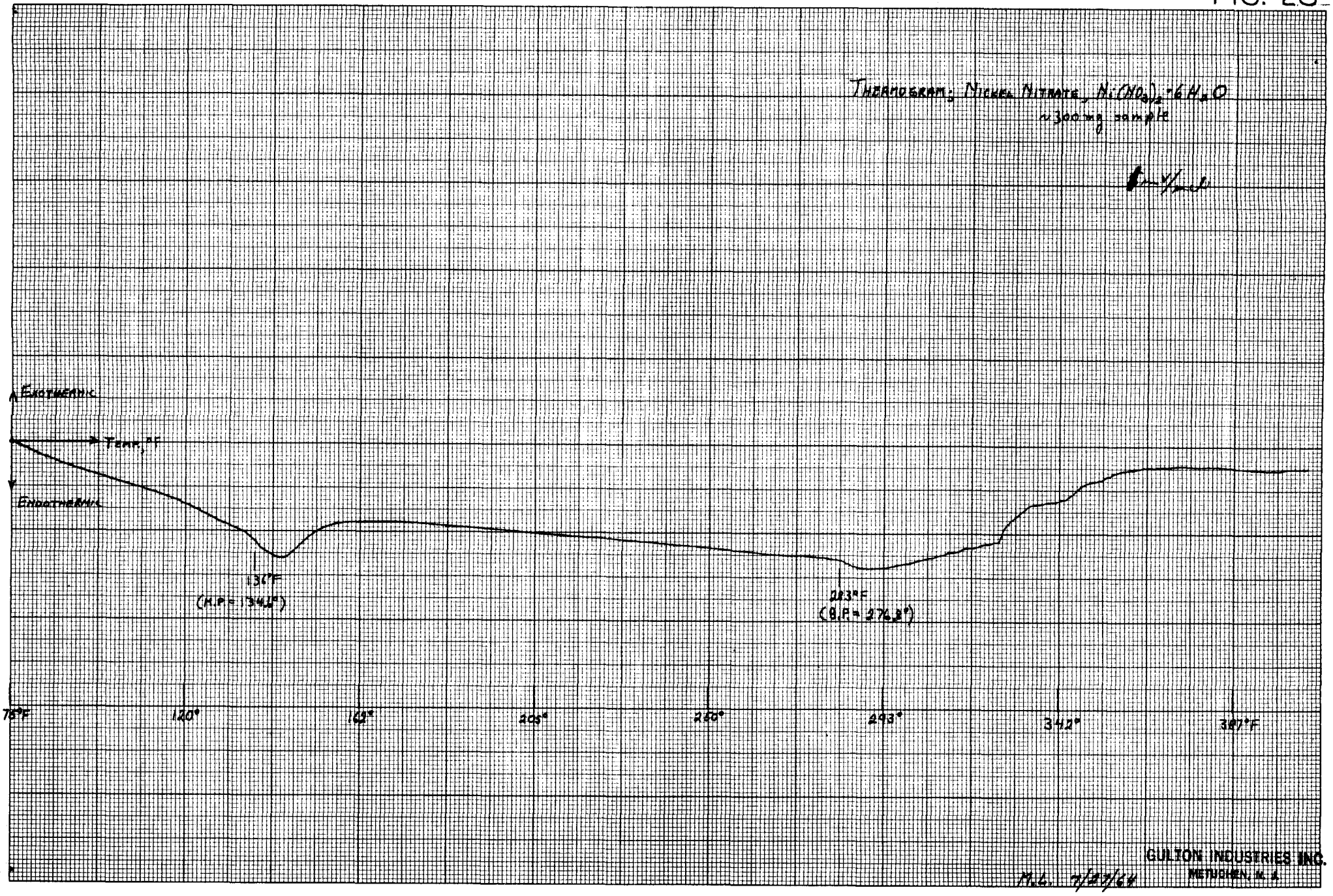

THERMOGRAM: NICKEL NITRATE, $Ni(NO_3)_2 \cdot 6H_2O$
~300 mg sample
EXOTHERMIC
TEMP. °F
ENDOTHERMIC
137°F
(M.P. = 134.6°)
283°F
(B.P. = 274.8°)
78°F
120°
162°
205°
250°
293°
342°
387°F
GULTON INDUSTRIES INC.
METUCHEN, N. J.
M.L. 7/27/64

FIG. 29

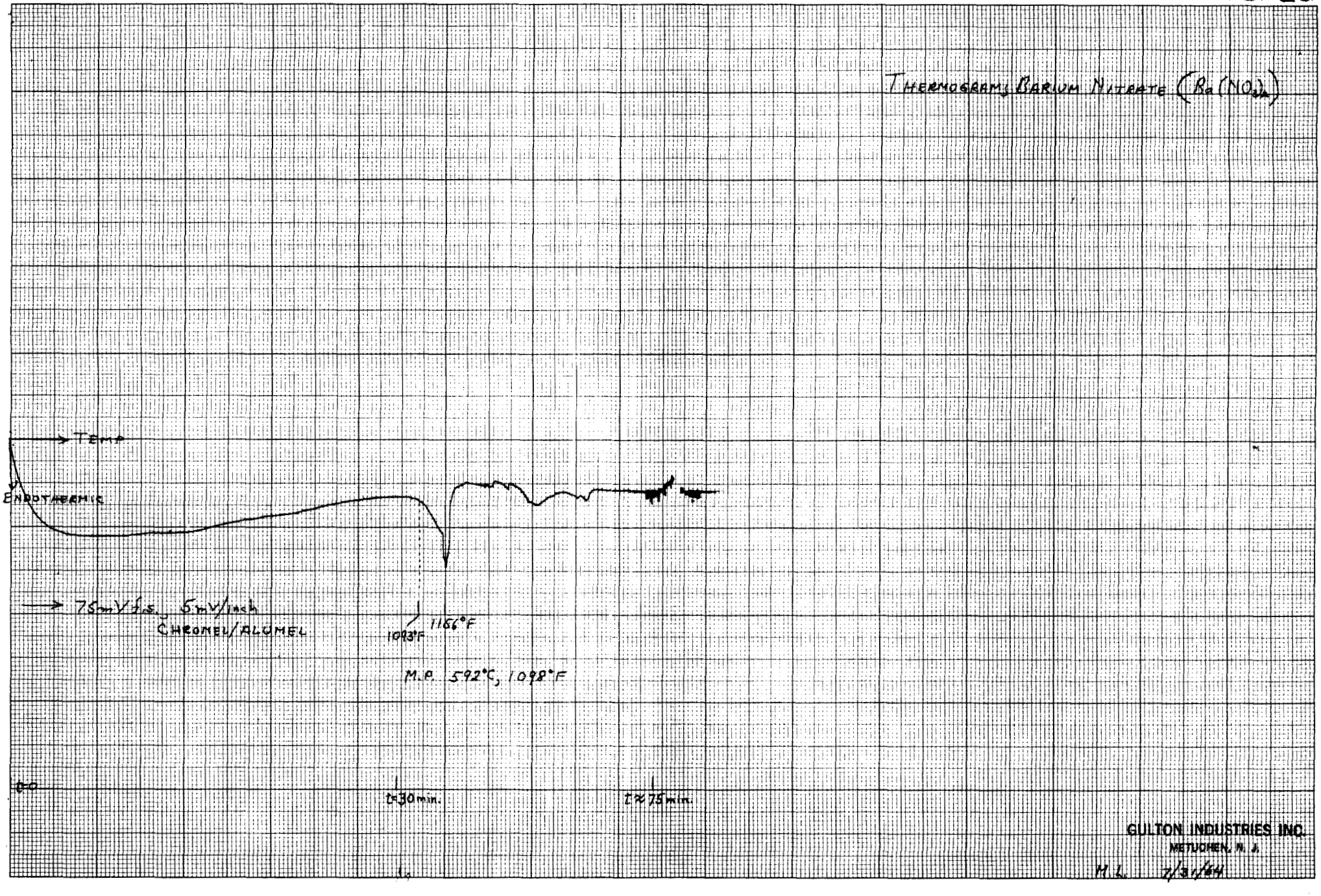

THERMOGRAM; BARIUM NITRATE ($Ba(NO_3)_2$)
TEMP
ENDOTHERMIC
75mV f.s., 5mV/inch
CHROMEL/ALUMEL
1093°F
1166°F
M.P. 592°C, 1098°F
t=30 min.
t≈75 min.
GULTON INDUSTRIES INC.
METUCHEN, N. J.
M.L. 7/31/64

FIG. 30

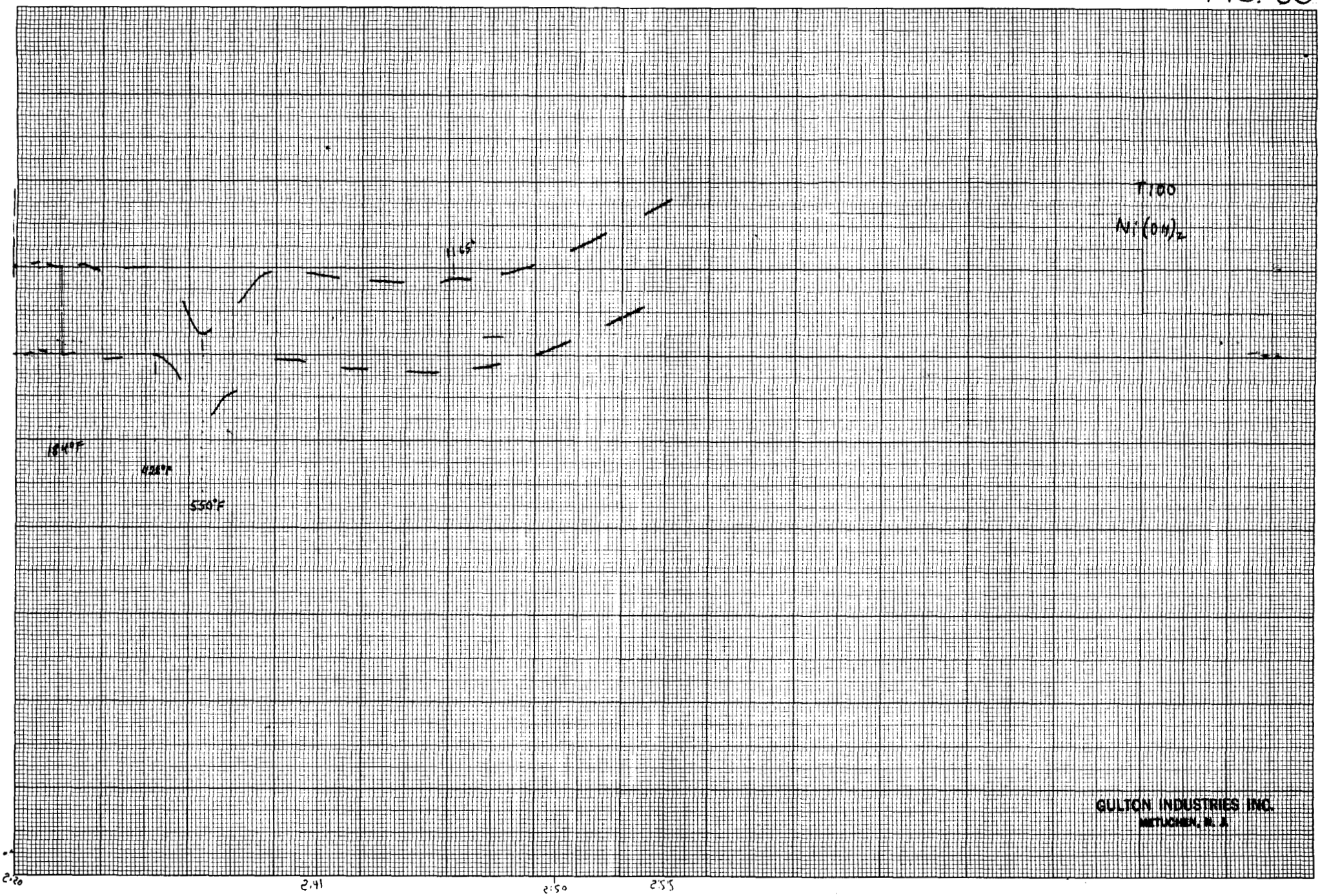
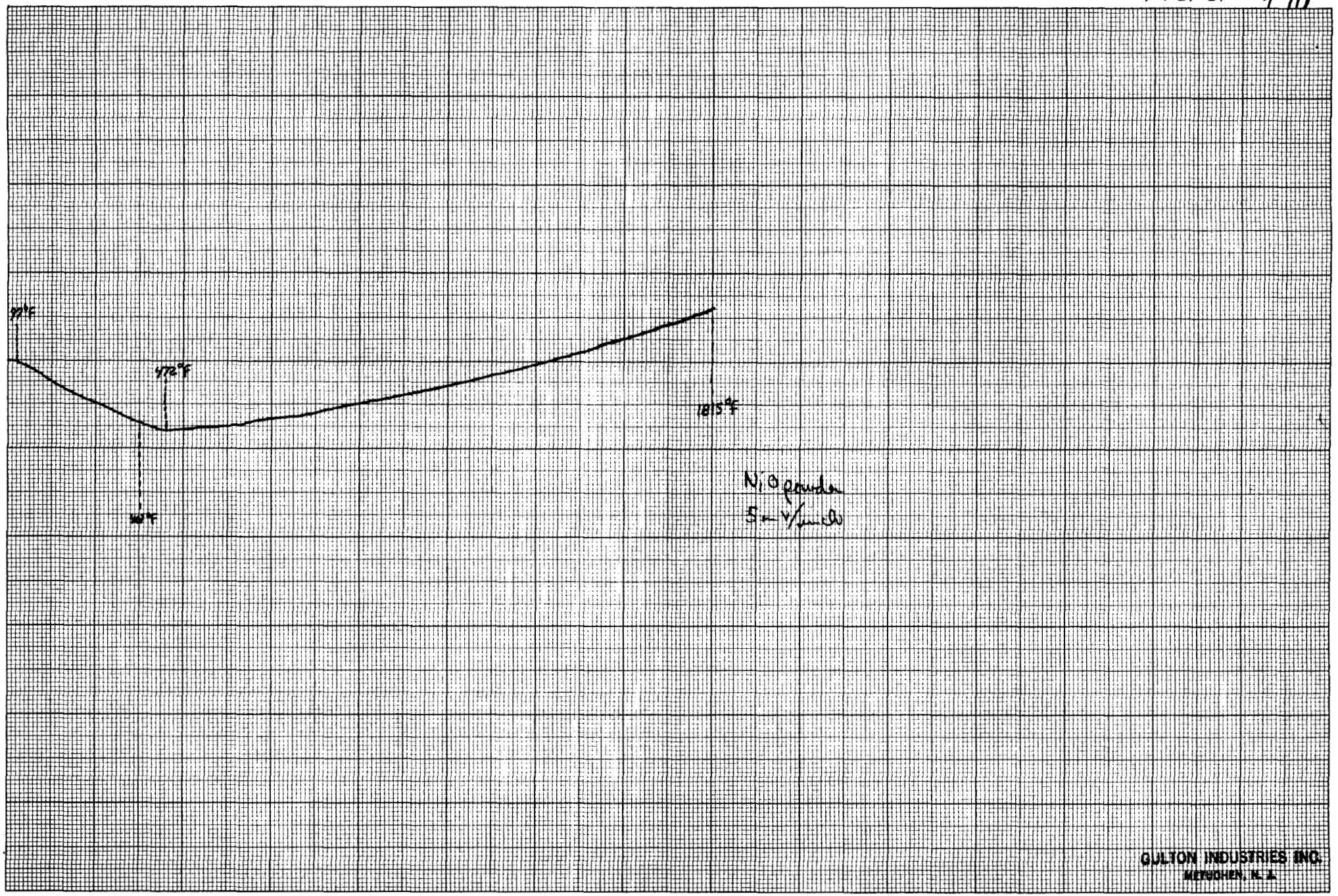

T100
Ni(OH)2
11:55
184°F
428°F
550°F
GULTON INDUSTRIES INC.
METUCHEN, N. J.
2:20
2:41
2:50
2:55

FIG. 31 T 117



9:14

S/G NiO FROM P. RITTERMAN

FIG. 32.

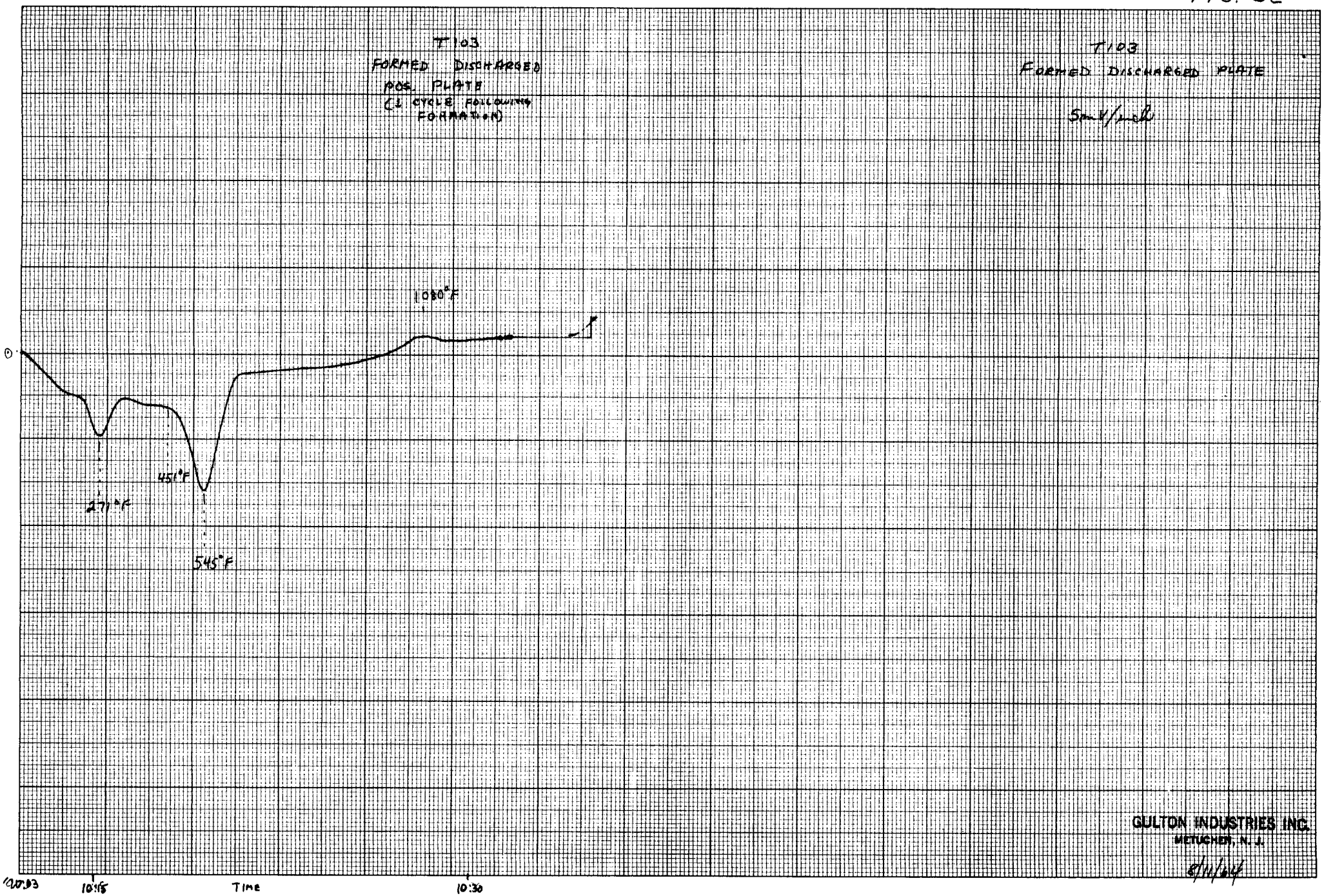
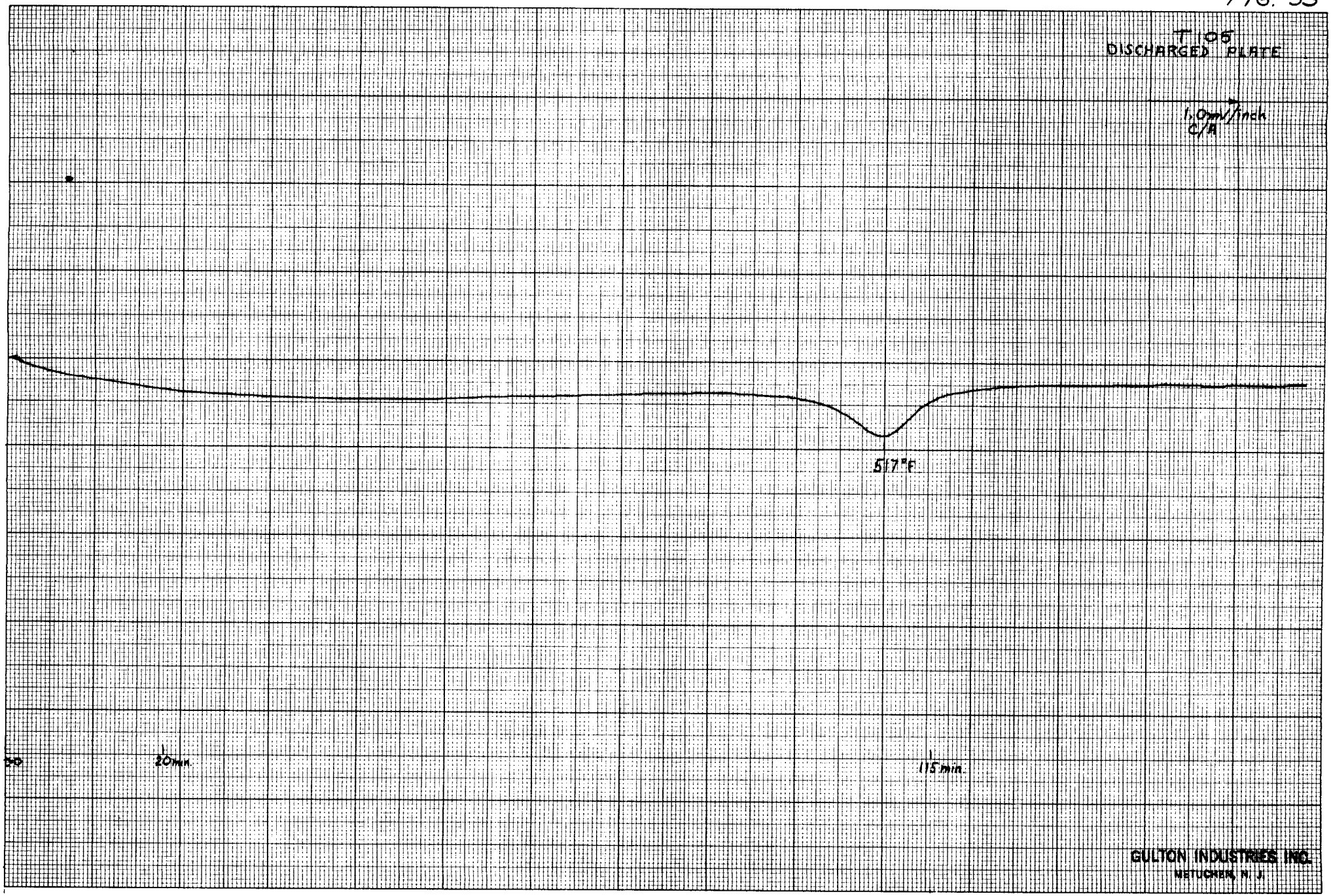

T103
FORMED DISCHARGED
POS. PLATE
(2 CYCLE FOLLOWING
FORMATION)
T103
FORMED DISCHARGED PLATE
5m V/inch
1080°F
0
451°F
271°F
545°F
GULTON INDUSTRIES INC.
METUCHEN, N. J.
8/11/64
10:03
10:15
TIME
10:30

FIG. 33


T 105
DISCHARGED PLATE
1.0mv/inch
C/A
517°F
20min.
115 min.
GULTON INDUSTRIES INC.
METUCHEN, N. J.

9135

FIG. 34

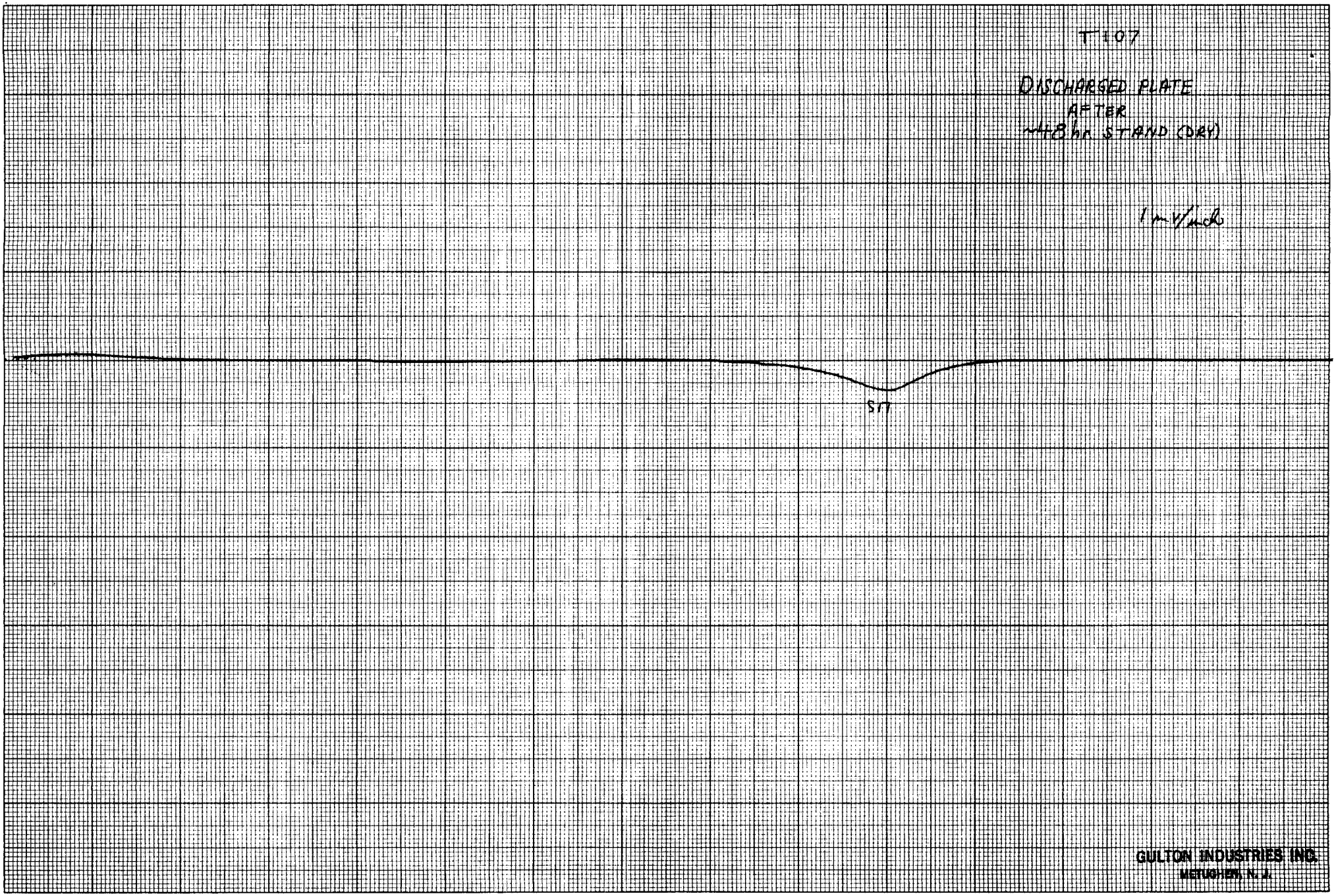

T107
DISCHARGED PLATE
AFTER
~48 hr. STAND (DRY)
1 mv/inch
S17
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIG. 35

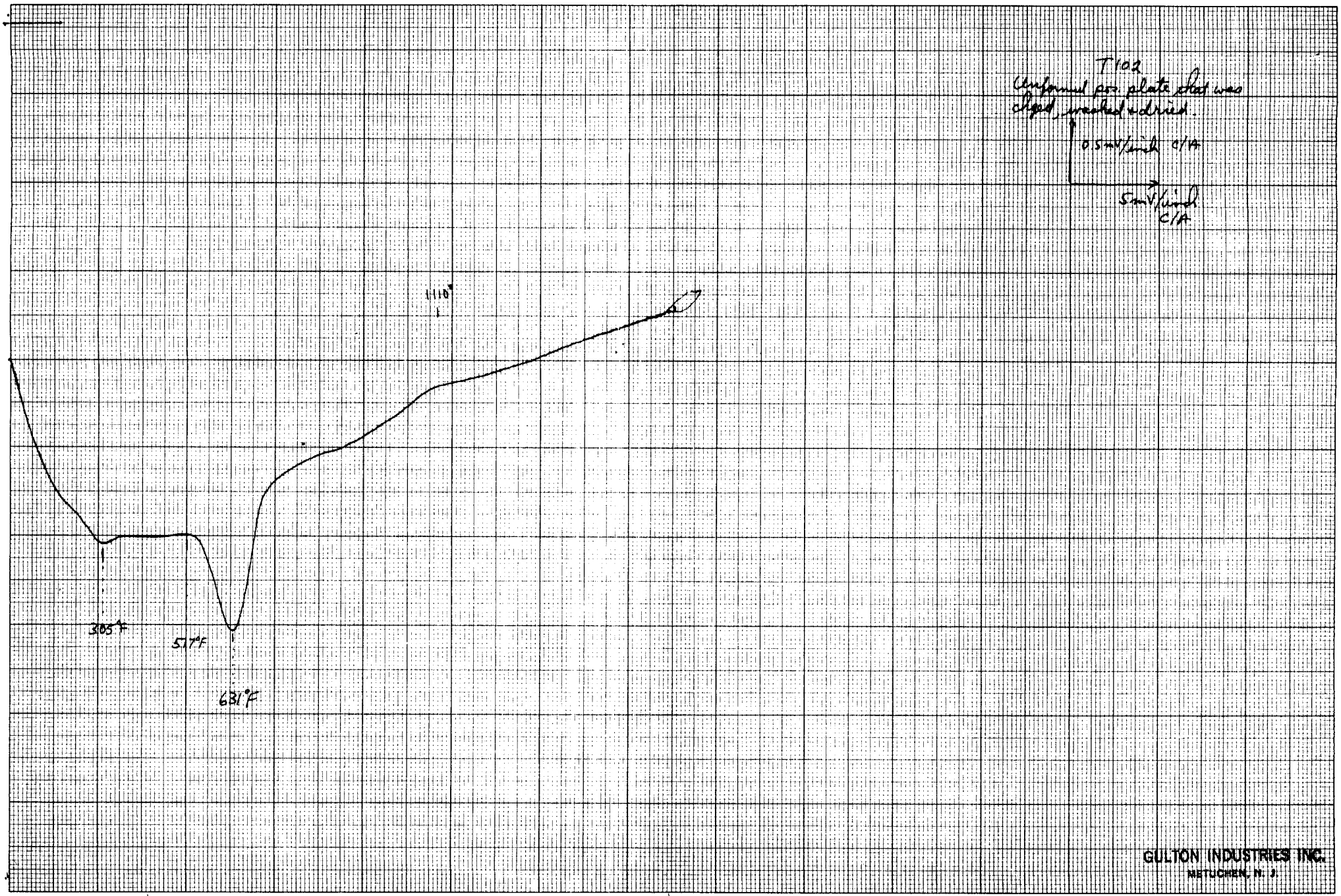
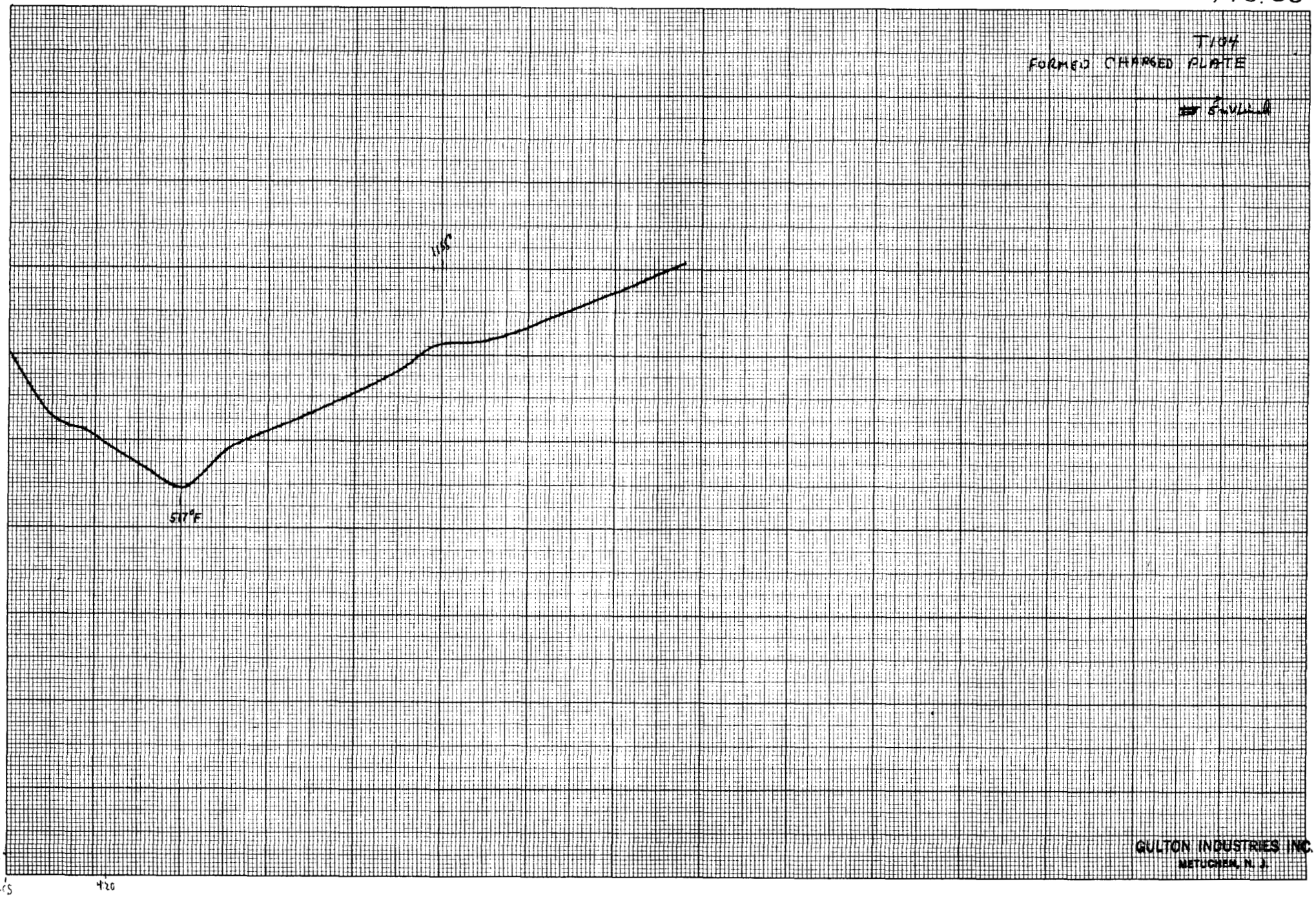

T102
Unformed pos. plate that was dried, wetted & dried.
0.5 mV/inch D/A
5 mV/inch C/A
1110°
305°F
517°F
631°F
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIG. 36



CHARGED PLATE

FIG. 37

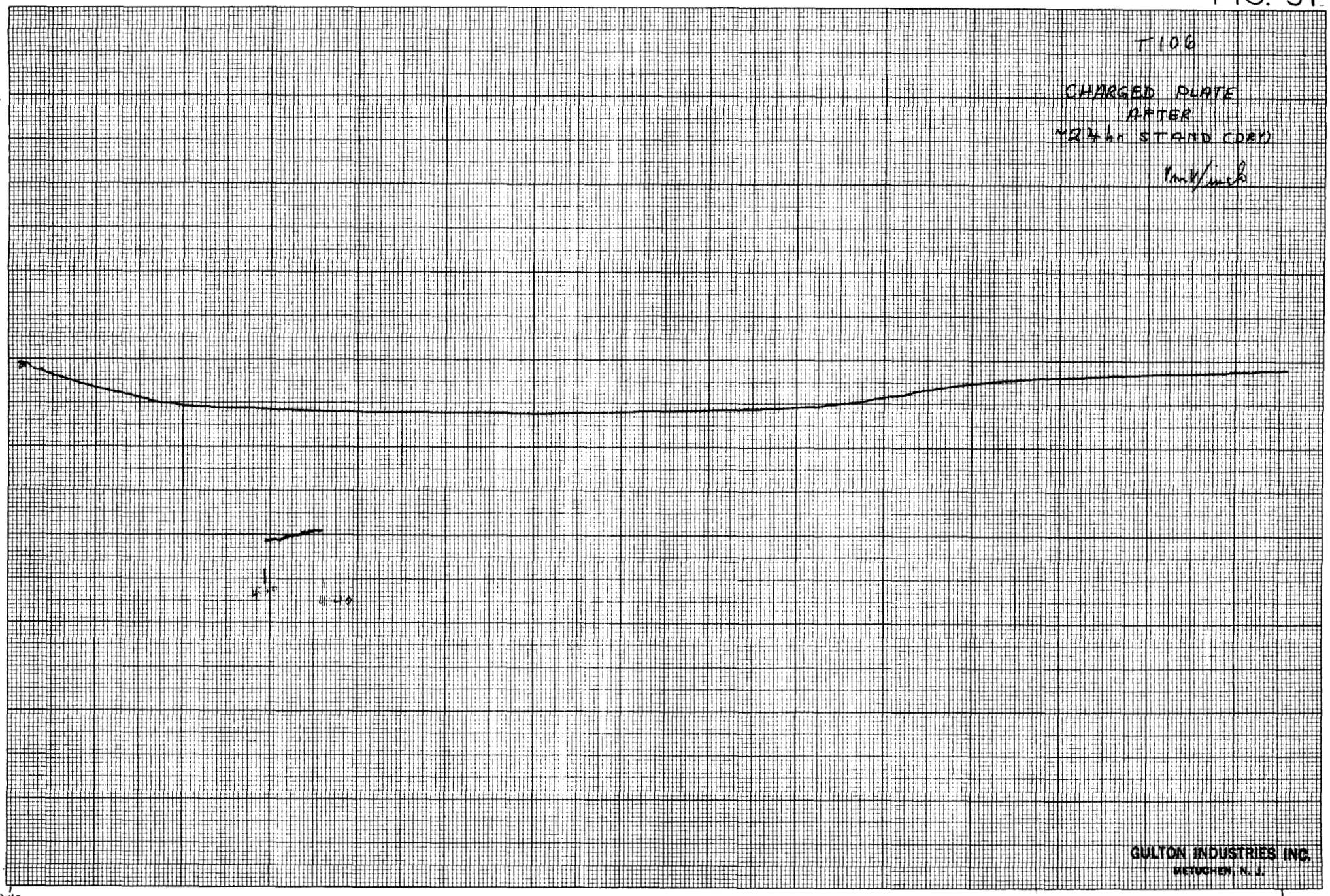
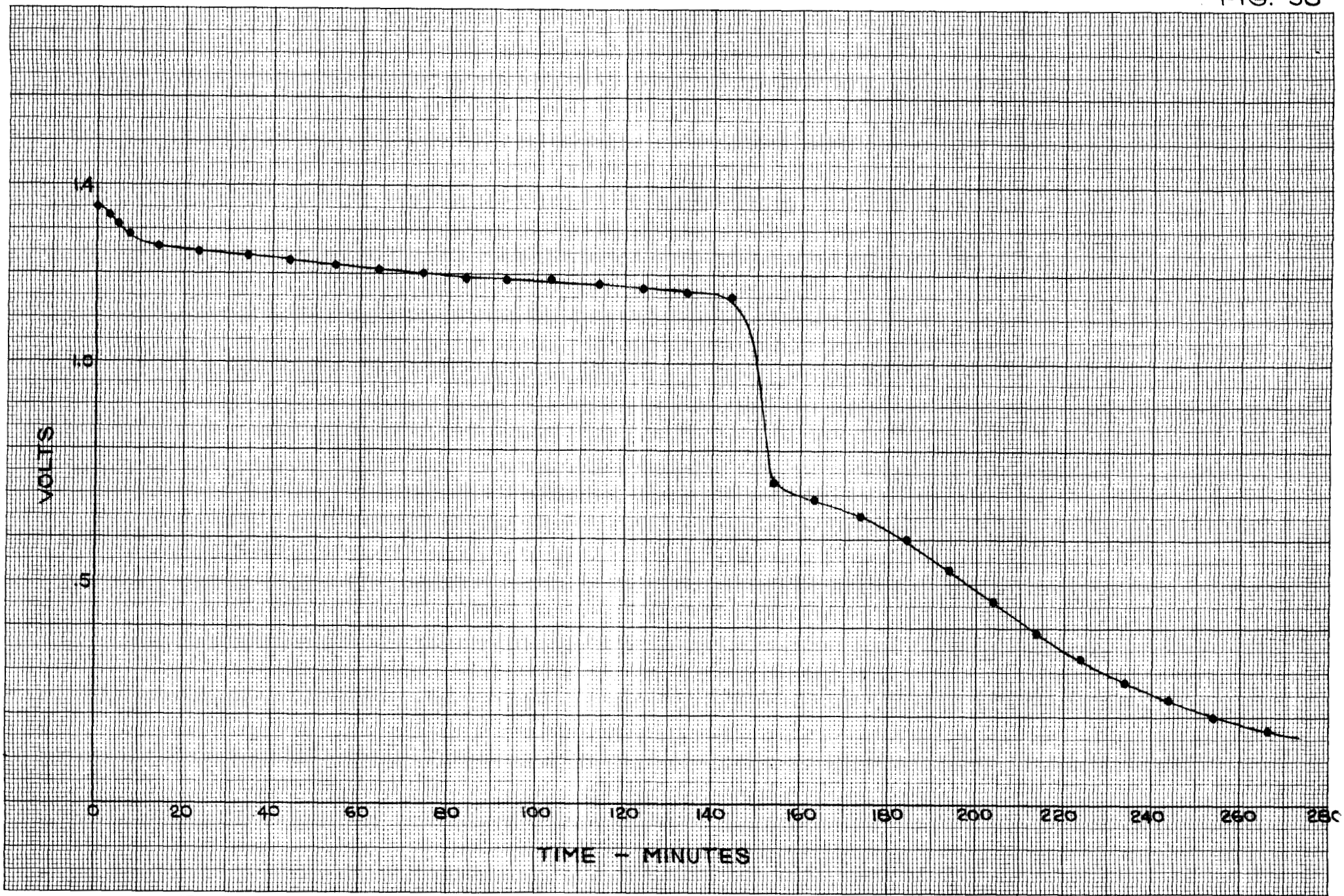

T106
CHARGED PLATE
AFTER
72 hr STAND (DRY)
1 mv/inch
GULTON INDUSTRIES INC.
METUCHEN, N. J.
2:40
3:40
4:00

FIG. 38



TYPICAL DISCHARGE CURVE CONSTANT LOAD = 2.4Ω
CELL 7, CYCLE 2

GULTON INDUSTRIES INC.
METUCHEN, N. J.

M2581
AB8400